GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L20821, doi:10.1029/2008GL035913, 2008

Nitrogen trifluoride in the global atmosphere

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Received 5 September 2008; revised 25 September 2008; accepted 3 October 2008; published 31 October 2008.

[1] Background atmospheric abundances and trends of nitrogen trifluoride (NF_3), a potent anthropogenic greenhouse gas, have been measured for the first time. The mean global tropospheric concentration of NF_3 has risen quasi-exponentially from about 0.02 ppt (parts-per-trillion, dry air mole fraction) at the beginning of our measured record in 1978, to a July 1, 2008 value of 0.454 ppt, with a rate of increase of 0.053 ppt yr^{-1}, or about 11% per year, and an interhemispheric gradient that is consistent with these emissions occurring overwhelmingly in the Northern Hemisphere, as expected. This rise rate corresponds to about 620 metric tons of current NF_3 emissions globally per year, or about 16% of the poorly-constrained global NF_3 production estimate of 4,000 metric tons yr^{-1}. This is a significantly higher percentage than has been estimated by industry, and thus strengthens the case for inventorying NF_3 production and for regulating its emissions. **Citation:** Weiss, R. F., J. Mühle, P. K. Salameh, and C. M. Harth (2008), Nitrogen trifluoride in the global atmosphere, *Geophys. Res. Lett.*, *35*, L20821, doi:10.1029/2008GL035913.

[2] Nitrogen trifluoride (NF_3) has come into increasing use in the electronics industry, mainly for equipment cleaning, for the etching of microcircuits, and for manufacturing liquid crystal flat panel displays and thin-film photovoltaic cells. As a replacement for perfluorocarbon (PFC) gases in these applications, NF_3 is largely destroyed during the manufacturing process, resulting in reduced emissions to the atmosphere [*Robson et al.*, 2006; *Lee et al.*, 2007]. On the other hand, the global warming potential (GWP) of NF_3 on a 100-year time horizon, about 17,000 times that of carbon dioxide, is greater than the GWPs of the PFCs it replaces and thus NF_3 has a greater impact on Earth's climate per unit mass of emissions [*Forster et al.*, 2007; *Prather and Hsu*, 2008]. NF_3 is not included in the Kyoto Protocol emissions restrictions or in national reporting under the United Nations Framework Convention on Climate Change (UNFCCC), making it an especially attractive PFC-substitute in Kyoto Protocol signatory nations. But based on a new assessment of its increased use and climate impact, and stressing the lack of verification for estimates of low industrial emissions, the addition of NF_3 to the list of regulated greenhouse gases in the second commitment period of the Kyoto Protocol recently has been recommended [*Prather and Hsu*, 2008], thus providing the incentive for the present first measurements of the actual accumulation of NF_3 in the atmosphere.

[3] We have measured NF_3 in nine samples of clean background Northern Hemisphere (NH) air collected between 1998 and 2008 at the Advanced Global Atmospheric Gases Experiment (AGAGE) station at Trinidad Head on the northern California coast (41.05°N, 124.15°W) and between 1978 and 1991 at La Jolla on the southern California coast (32.87°N, 117.25°W), and in two samples of clean background Southern Hemisphere (SH) air collected in 1995 and 2005 at the AGAGE station at Cape Grim, Tasmania (40.68°S, 144.69°E). These stored samples were selected for NF_3 analysis on the basis of the high integrity they have shown for measurements of other volatile trace gases with well-known atmospheric trends.

[4] NF_3 was measured using a modified version of the Medusa cryogenic preconcentration and gas chromatograph/mass spectrometer (GC/MS) system [*Miller et al.*, 2008], using *m*/*z* of 52 as the quantifying ion and 71 and 33 as qualifying ions. Critically, NF_3 must be separated in the GC/MS from more abundant volatile atmospheric gases, especially krypton (Kr) and carbon dioxide (CO_2), to avoid quenching the mass spectrometer with these far more abundant gases. NF_3 is similar in volatility to carbon tetrafluoride (CF_4), but because trace amounts of NF_3 are trapped irreversibly in the molecular sieves 4Å, 5Å and HiSiv-3000 pre-column adsorbents that have been used to separate CF_4 from these interfering gases in the Medusa, we did not use a pre-column. Instead, we removed CO_2 from samples and standards with Ascarite CO_2 absorbent and separated Kr from NF_3 by optimizing the fractional distillation temperatures and flows during transfer of the sample between the two traps in the preconcentration system. The CP-PoraBOND Q main column was maintained at 28°C, and the later-eluting gases normally measured by the Medusa were purged to waste directly from the first trap without injection onto the main column.

[5] Calibration was achieved with a 3.42 ppt (parts-per-trillion, dry air mole fraction) NF_3 standard prepared from pure NF_3 using the "bootstrap" method used in AGAGE [*Prinn et al.*, 2000], except that the NF_3 in the initial mixture of NF_3 in nitrous oxide (N_2O) was quantified volumetrically. To minimize potential biases due to Kr and other atmospheric constituents, primary calibration was achieved by the method of internal additions. The prepared NF_3/N_2O mixture was diluted with real air and the resulting increases in N_2O and NF_3 were measured relative to the original diluent air using AGAGE methods and standards [*Prinn et al.*, 2000] for N_2O and the modified Medusa for NF_3. We estimate that our NF_3 primary calibration is accurate to about 2%. Measurement precisions for our replicate samples are given in Table 1. The NF_3 detection limit is about 0.004 ppt.

[6] The results of our NF_3 measurements are listed in Table 1 and plotted in Figure 1a. In the NH, where the trend is clearly established by the higher sampling density, the

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0094-8276/08/2008GL035913$05.00

Table 1. Mean Measured NF_3 Concentrations in Clean Background Air[a]

Sample Date	Location	NF_3 (ppt)	SD (ppt)	n
12 Mar 2008	TH	0.478	0.006	4
20 Mar 2007	TH	0.422	0.006	6
6 Feb 2006	TH	0.367	0.016	9
14 Mar 2005	TH	0.327	0.012	4
20 Apr 2003	TH	0.246	0.010	3
31 Jan 1998	TH	0.102	0.006	4
24 Mar 1991	LJ	0.036	0.002	3
19 Jan 1980	LJ	0.022	0.004	4
10 Aug 1978	LJ	0.015	0.003	5
1 Jun 2005	CG	0.277	0.015	2
23 Nov 1995	CG	0.059	0.003	4

[a] TH, Trinidad Head, California (41.05°N, 124.15°W); LJ, La Jolla, California (32.87°N, 117.25°W); CG, Cape Grim, Tasmania (40.68°S, 144.69°E); SD, standard deviation; and n, number of replicates. Samples were stored in electropolished stainless steel high-pressure canisters, except those collected prior to 1992, which were stored in silanized aluminum high-pressure cylinders.

data show a quasi-exponential growth, and in the SH, where the sampling is too sparse to establish an independent trend, the data nonetheless lag the NH trend, as is expected because the industrial uses of NF_3 are overwhelmingly in the NH [*Hoag*, 2008; *Prather and Hsu*, 2008].

[7] The results are modeled with a simple two-box representation of the NH and SH troposphere which assumes that the measurements are representative of their respective hemispheres and which is driven by the measured NH trend. As noted in Table 1, the NH measurements come from two California coastal sites. Based on the excellent agreements between these sites for real-time AGAGE measurements of a wide range of long-lived trace gases in clean background air [*Prinn et al.*, 2000; *Miller et al.*, 2008] we are confident in combining our NF_3 measurements into a single 30-year NH record. The much sparser SH measurements are used only to verify the modeled SH results. The interhemispheric exchange rate τ_{IH} is taken as 1.5 yr, and the atmospheric lifetime τ_L is taken as 550 yr [*Prather and Hsu*, 2008]. Accordingly, changes in the concentration C in either hemisphere are governed by the equation:

$$\frac{dC_i}{dt} = \varphi_i - \frac{C_i - C_j}{\tau_{IH}} - \frac{C_i}{\tau_L}$$

where t is time, φ is the emissions flux into the respective hemisphere in concentration units per unit t, and the subscripts i and j refer to the two hemispheres interchangeably. We assume in this calculation that all of the emissions are confined to the NH, so that φ_{SH} is zero, and we solve for C_{SH} and φ_{NH} by numerical integration using the spline curve fitted to C_{NH} that is plotted in Figure 1a. For the SH initial condition we assume that C_{SH} lags C_{NH} by τ_{IH} at the beginning of the record. To convert atmospheric fluxes and burdens from concentration units to mass units, we take the number of moles of dry air in the global troposphere as 1.67×10^{20} moles, divided equally between the two hemispheres.

[8] The results of the NF_3 model calculation are plotted in Figure 1, where the modeled SH and global mean concentration trends are shown alongside the measured NH trend, and the two SH measurements are shown to be in good agreement with the modeled SH trends. These results yield a July 1, 2008 mean global tropospheric concentration of 0.454 ppt that is increasing at 0.053 ppt yr^{-1}, and corresponds to a global tropospheric burden of 5,380 metric tons of NF_3 that is increasing at about 11% per year. As is also shown in Figure 1, the mean global tropospheric concentration of NF_3 has risen from a value of about 0.02 ppt at the beginning of our measured record in 1978. NF_3 is known to have been used as early as the 1960s in specialty applications such as as a rocket fuel oxidizer [*Bronfin and Hazlett*, 1966], so we can say only that if there is a pre-industrial natural background of NF_3 in the atmosphere it is less than 0.02 ppt. Plotted in Figure 1b is the annual global (and NH) flux of NF_3 into the atmosphere, showing a value that has risen from about 110 metric tons yr^{-1} in 1995 to about 620 metric tons yr^{-1} in 2008.

[9] These first measured values of NF_3 in the global atmosphere show significantly higher current concentrations than have been predicted based on limited industrial production data and estimates of NF_3 destruction in electronics applications. If the current 2008 global production of NF_3 is 4,000 ± 1,000 metric tons yr^{-1} [*Prather and Hsu*, 2008], our mid-2008 modeled global emission of 620 metric tons yr^{-1} corresponds to 16 ± 4% of production. In 2006 it was estimated that emissions were 140 metric tons yr^{-1} [*Robson et al.*, 2006] based on 85% of 2300 metric tons yr^{-1} production being used in electronics applications with

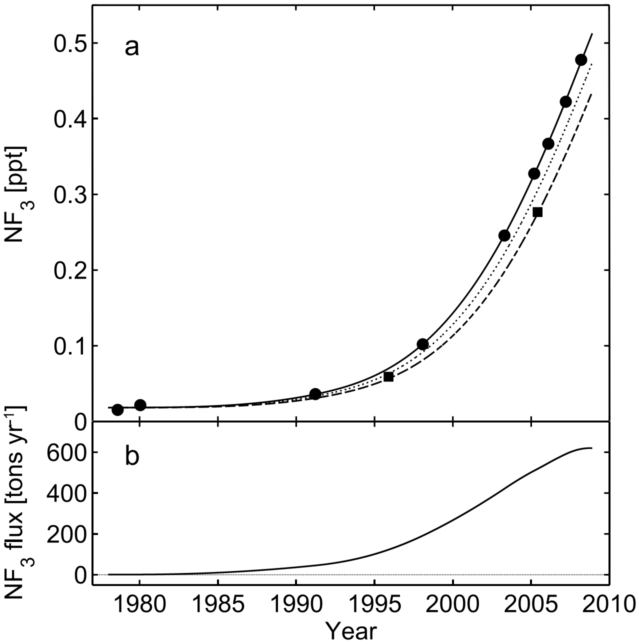

Figure 1. Measured and modeled atmospheric NF_3 concentrations and trends from 1978 to 2008. (a) Northern Hemisphere NF_3 measurements (ppt, dry air mole fraction) are shown as filled circles, together with the spline curve Northern Hemisphere trend (solid line) fitted to these measurements. The modeled Southern Hemisphere trend and modeled global mean trend are shown as dashed and dotted lines, respectively. Southern Hemisphere measurements are plotted as filled squares. (b) Modeled global NF_3 emissions flux in metric tons per year for the same time period.

2% emissions, and 15% of production being used in applications with 30% emissions that were being phased out. By comparison, our mean modeled 2006 emission rate is 563 metric tons yr^{-1}, a factor of four higher. We note that the slight leveling off of the emissions curve in Figure 1b over the last few years is inconsistent with the dramatic rise in the production of flat panel displays and other uses of NF_3 in electronics during this period [*Hoag*, 2008]. This suggests that some leveling off may be due to a combination of increased efficiency in the destruction of NF_3 in electronics applications as well as the phasing out of higher emissions applications. In any case, it seems unlikely that the present rate of NF_3 emissions in the electronics industry is limited to the often-quoted value of 2%, or even 3%, of production [*Lee et al.*, 2007; *Hoag*, 2008], or that emissions will not eventually continue to rise without improved measures to reduce current electronics industry emissions percentages. Given the large uncertainty in the present global NF_3 production rate and the high GWPs [*Forster et al.*, 2007] of NF_3 and of the PFCs it replaces in electronics applications, the steep percentage rise we observe in the abundance of NF_3 in the global atmosphere provides essential validation for the recent recommendation [*Prather and Hsu*, 2008] that NF_3 be added to the list of perfluorinated greenhouse gases whose production is inventoried and whose emissions are regulated in the second commitment period of the Kyoto Protocol.

[10] **Acknowledgments.** We thank F. A. Van Woy and the late L. W. Porter for collecting most of the California air samples, and the two Cape Grim air samples, respectively, measured in this study. This research was supported by NASA through the Upper Atmosphere Research Program, Earth Science Division, as part of the AGAGE program.

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