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NF_3, the greenhouse gas missing from Kyoto

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[1] Nitrogen trifluoride (NF_3) can be called the missing greenhouse gas: It is a synthetic chemical produced in industrial quantities; it is not included in the Kyoto basket of greenhouse gases or in national reporting under the United Nations Framework Convention on Climate Change (UNFCCC); and there are no observations documenting its atmospheric abundance. Current publications report a long lifetime of 740 yr and a global warming potential (GWP), which in the Kyoto basket is second only to SF_6. We reexamine the atmospheric chemistry of NF_3 and calculate a shorter lifetime of 550 yr, but still far beyond any societal time frames. With 2008 production equivalent to 67 million metric tons of CO_2, NF_3 has a potential greenhouse impact larger than that of the industrialized nations' emissions of PFCs or SF_6, or even that of the world's largest coal-fired power plants. If released, annual production would increase the lower atmospheric abundance by 0.4 ppt, and it is urgent to document NF_3 emissions through atmospheric observations. **Citation:** Prather, M. J., and J. Hsu (2008), NF_3, the greenhouse gas missing from Kyoto, *Geophys. Res. Lett.*, *35*, L12810, doi:10.1029/2008GL034542.

[2] The Kyoto Protocol to the UNFCCC was based on the 1995 scientific assessment of the *Intergovernmental Panel on Climate Change* (*IPCC*) [1996]. The Kyoto basket (Annex A) includes the big-three, natural greenhouse gases - CO_2, CH_4, N_2O - whose increases over the industrial era can be ascribed to human activities. It also includes synthetically produced greenhouse gases categorized by name like sulfur hexafluoride (SF_6) or by class like the hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). Nitrogen trifluoride (NF_3) does not fall under any of the Kyoto categories, in part because its potential importance as a greenhouse gas was not evaluated until the 2001 IPCC assessment [*Ramaswamy et al.*, 2001]. Like other specialty chemicals, NF_3 began as a niche product, in this case for rocket fuel and lasers. Now, it is marketed as a plasma etchant and equipment cleaning gas in the semiconductor industry. With the surge in demand for flat panel displays, the market for NF_3 has exploded. Air Products has just announced a major expansion of NF_3 manufacturing facilities in the USA and Korea to annual production of 3,200 tons by 2009 (Air Products boosts NF_3 capacity in U.S. and Asia, Air Products press release of 27 November 2007, available at http://www.airproducts.com/PressRoom/CompanyNews/Archived/2007/27Nov2007.htm). While Air Products is the acknowledged single largest NF_3 producer, others in the chemical industry are following: Kanto Denka produces 1,000 tons per yr; DuPont is setting up a manufacturing facility in China; Formosa Plastics and Mitsui Chemicals are expanding production. Data on total production is not freely available, but based on press releases and industry data, we estimate 2008 production to be about 4,000 tons, with a likely range of ±25%. Planned expansion could double this by 2010.

[3] The published global warming potentials (GWP) of NF_3 are 12,300, 17,200 and 20,700 for time horizons of 20, 100, and 500 years, respectively [*Forster et al.*, 2007]. The increasing GWP with time horizon reflects the longer atmospheric residence time of NF_3 compared with that of CO_2. Compared to the Kyoto-listed gases, the GWP is second only to that of SF_6 (100-yr GWP = 22,800). On a per molecule basis, the radiative efficiency of NF_3 is high, 0.21 W m^{-2} per ppb [*Robson et al.*, 2006], placing near the top of the low-molecular weight HFCs and between CF_4 (0.10) and C_2F_6 (0.26). The published GWP is derived from the radiative efficiency and an atmospheric lifetime based solely on photolysis [*Molina et al.*, 1995]. Including reaction of $O(^1D)$ with NF_3 at a rate coefficient of 1.15×10^{-11} cm^3 s^{-1} [*Sorokin et al.*, 1998] will reduce its lifetime. We recalculate it here with a modern 3-D chemistry transport model [*Olsen et al.*, 2001; *Wild and Prather*, 2006]. For perspective, we also recalculate the lifetimes of the major chlorofluorocarbons. Following *Avallone and Prather* [1997], the loss frequencies of NF_3 and the CFCs are calculated off-line for 12 months, 18 latitudes, and 25 pressure levels using climatologies for O_3 and temperature. For NF_3, we adopt the *Molina et al.* [1995] cross sections, which have no dependence on temperature. For the CFCs we used the IUPAC data sheets (International Union of Pure and Applied Chemistry Subcommittee on Gas Kinetic Data Evaluation, 18 May 2004, available at http://www.iupac-kinetic.ch.cam.ac.uk/) and interpolate linearly with temperature between the 210 K and 298 K tables. For CFC-115 there is no recommended temperature dependence.

[4] The CTM uses meteorological fields for year 2005 from the European Centre for Medium-range Weather Forecasting [*Wild et al.*, 2003; *Hsu et al.*, 2005] at resolution T42L60 with a top at 0.1 hPa. With a fixed, uniform tracer abundance in the lowest 4 layers, the CTM is integrated for 10 model-years, and the atmospheric budget lifetimes are calculated as the mean burden in year 10 divided by the accumulated annual loss (see Table 1). The calculation is in near steady state, where differences between years 9 and 10 are negligible. Our lifetimes are computed both with and without $O(^1D)$ reactions and compared with the reference lifetimes published in IPCC [*Forster et al.*, 2007].

[5] The new NF_3 lifetime, 550 yr, is shorter by about 25%, with half of the decrease due to inclusion of the $O(^1D)$ reaction. With this new lifetime, the 100-yr GWP drops slightly from 17,200 to 16,800, and NF_3 remains a potent

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greenhouse gas. (The updated 20-yr GWP is 12,200, and 500-yr GWP is 18,700.)

[6] The new lifetimes for CFC-11, -12, and -113 are very close to the reference lifetimes, but those for -114 and -115 are shorter by factors of 2 and 3, respectively. The cause of such large differences is not obvious. The CFC-114 cross sections at 210 K used here from IUPAC tables are much less than the 298 K values (i.e., giving a longer lifetime) and agree with the polynomial formula in JPL tables [*Sander et al.*, 2006]. For CFC-115 there is no recommendation in either IUPAC or JPL for reduced cross sections at lower temperatures. One possibility is that $O(^1D)$ losses were not included, and indeed our CTM without $O(^1D)$ nearly matches the reference lifetimes for CFC-114 and -115. These lifetimes will need to be revisited and likely revised for the next WMO/UNEP ozone assessment in 2010.

[7] While NF_3 is ostensibly destroyed during the manufacture of flat screen displays, this destruction cannot be complete. We expect that some fraction of the NF_3 produced will escape to the atmosphere during production, transport, use, or disposal. The maximum potential release of NF_3, assumed here to be its production, is equivalent to approximately 67 $MMTCO_2$ (million metric tons of CO_2, see Table 2). Thus, in terms of climate change, annual production of NF_3 is now larger than emissions of PFCs or SF_6 reported by the developed nations (Annex I) for 2005. (See Table 2; note that these emissions are generally decreasing since 1990.) NF_3 production is about 6% of N_2O emissions and about $^1/_2$% of CO_2 emissions (UNFCCC, 2007 Greenhouse Gas Emissions data are available at http://unfccc.int/ghg_emissions_data/ghg_data_from_unfccc/time_series_annex_i/items/3814.php). For perspective, NF_3 production projected for next year by one company alone (Air Products) will reach the equivalent of 54 $MMTCO_2$, exceeding the world's largest coal-fired power stations (e.g., 25 to 32 $MMTCO_2$, see http://carma.org and Table 2).

[8] NF_3 is an expensive commodity with an estimated price of about $US 20 per kg, and thus there are economic as well as environmental incentives not to waste it through inadvertent release. According to *Robson et al.* [2006], most of NF_3 is used in a manner such that only 2% escapes to the atmosphere, but this contrasts with studies by *Lee et al.* [2007] showing a maximum destruction efficiency of less than 97% under ideal conditions. Moreover, there is an economic incentive, a tradeoff between more efficient NF_3 destruction and faster throughput [*Pruette et al.*, 1999], which encourages greater emissions. These emission fractions for NF_3 do not include fugitive release during its manufacture, transport, application, or disposal.

Table 1. Atmospheric Budget Lifetimes of Fluorinated Gases From UCI CTM With and Without $O(^1D)$ Reactions Compared With IPCC[a]

Gas	UCI Without $O(^1D)$	UCI With $O(^1D)$	IPCC
NF_3	640	550	740
CFC-11 ($CFCl_3$)	48	47	45
CFC-12 (CF_2Cl_2)	100	96	100
CFC-113 ($CF_2ClCFCl_2$)	82	80	85
CFC-114 (CF_2ClCF_2Cl)	230	180	300
CFC-115 (CF_3CF_2Cl)	1650	540	1700

[a] Source: *Forster et al.* [2007]. Lifetimes are given in years.

Table 2. Annual Production or Emissions of Greenhouse Gases

	Equivalent Million Metric Tons of CO_2 ($MMTCO_2$) Equivalent[a]
2008 Worldwide Production	
NF_3	67
2005 Annex-I Emissions	
SF_6	35
PFCs	42
HFCs	232
N_2O[b]	1,130
CH_4[b]	1,615
CO_2[b]	15,128
3600 MW Coal-Fired Plants	
Scherer (Georgia, USA)	25
Tuoketuo-1 (Inner Mongolia, China)	32

[a] Mass weighted by 100-yr GWP.

[b] Without land-use change and forestry.

[9] Experience with the ozone-depleting gas CFC-12 [*Rowland et al.*, 1982] has shown that emission inventories from the chemical industry cannot be relied upon. Once released to the atmosphere, gases like CFC-12 and NF_3 will take centuries to clean out. Given this potential, the production of high-GWP, long-lived, greenhouse gases like NF_3 should be included in the national greenhouse gas inventories once global usage exceeds a threshold, e.g., 5 $MMTCO_2$, no matter what the claim for containment. Returning to the intent of UNFCCC Article 3.3 ("... policies and measures should ... cover all relevant sources, sinks and reservoirs of greenhouse gases ..."), it seems prudent to expand the list of greenhouse gases for the second commitment period of the Kyoto Protocol.

[10] Current production, if released, would add about 0.4 ppt (picomoles per mole) of NF_3 to the lower atmosphere annually. There appear to be no reported atmospheric measurements in the peer-reviewed literature [*Harnisch et al.*, 2000], and it is important to document the rise in atmospheric NF_3 that is almost certainly occurring today.

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