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NF₃, the greenhouse gas missing from Kyoto

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[1] Nitrogen trifluoride (NF₃) 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 SF₆. We re-examine the atmospheric chemistry of NF₃ 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 CO₂, NF₃ has a potential greenhouse impact larger than that of the industrialized nations' emissions of PFCs or SF₆, 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 NF₃ emissions through atmospheric observations. **Citation:** Prather, M. J., and J. Hsu (2008), NF₃, 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 - CO₂, CH₄, N₂O - 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 (SF₆) or by class like the hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). Nitrogen trifluoride (NF₃) 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, NF₃ 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 NF₃ has exploded. Air Products has just announced a major expansion of NF₃ manufacturing facilities in the USA and Korea to annual production of 3,200 tons by 2009 (Air Products boosts NF₃ 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 NF₃ 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 $\pm 25\%$. Planned expansion could double this by 2010.

[3] The published global warming potentials (GWP) of NF₃ 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 NF₃ compared with that of CO₂. Compared to the Kyoto-listed gases, the GWP is second only to that of SF₆ (100-yr GWP = 22,800). On a per molecule basis, the radiative efficiency of NF₃ 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 CF₄ (0.10) and C₂F₆ (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 NF₃ at a rate coefficient of 1.15×10^{-11} cm³ 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 NF₃ and the CFCs are calculated off-line for 12 months, 18 latitudes, and 25 pressure levels using climatologies for O₃ and temperature. For NF₃, 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 NF₃ 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 NF₃ 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 NF₃ is ostensibly destroyed during the manufacture of flat screen displays, this destruction cannot be complete. We expect that some fraction of the NF₃ produced will escape to the atmosphere during production, transport, use, or disposal. The maximum potential release of NF₃, assumed here to be its production, is equivalent to approximately 67 MMTCO₂ (million metric tons of CO₂, see Table 2). Thus, in terms of climate change, annual production of NF₃ is now larger than emissions of PFCs or SF₆ reported by the developed nations (Annex I) for 2005. (See Table 2; note that these emissions are generally decreasing since 1990.) NF₃ production is about 6% of N₂O emissions and about 1/2% of CO₂ 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, NF₃ production projected for next year by one company alone (Air Products) will reach the equivalent of 54 MMTCO₂, exceeding the world's largest coal-fired power stations (e.g., 25 to 32 MMTCO₂, see <http://carma.org> and Table 2).

[8] NF₃ 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 NF₃ 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 NF₃ destruction and faster throughput [Pruette *et al.*, 1999], which encourages greater emissions. These emission fractions for NF₃ 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(¹ D)	UCI With O(¹ D)	IPCC
NF ₃	640	550	740
CFC-11 (CFCl ₃)	48	47	45
CFC-12 (CF ₂ Cl ₂)	100	96	100
CFC-113 (CF ₂ ClCFCl ₂)	82	80	85
CFC-114 (CF ₂ ClCF ₂ Cl)	230	180	300
CFC-115 (CF ₃ CF ₂ Cl)	1650	540	1700

^aSource: 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
<i>2008 Worldwide Production</i>	
NF ₃	67
<i>2005 Annex-I Emissions</i>	
SF ₆	35
PFCs	42
HFCs	232
N ₂ O ^b	1,130
CH ₄ ^b	1,615
CO ₂ ^b	15,128
<i>3600 MW Coal-Fired Plants</i>	
Scherer (Georgia, USA)	25
Tuoketuo-1 (Inner Mongolia, China)	32

^aMass weighted by 100-yr GWP.

^bWithout 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 NF₃ will take centuries to clean out. Given this potential, the production of high-GWP, long-lived, greenhouse gases like NF₃ should be included in the national greenhouse gas inventories once global usage exceeds a threshold, e.g., 5 MMTCO₂, 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 NF₃ 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 NF₃ that is almost certainly occurring today.

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