Nitrogen trifluoride global emissions estimated from updated atmospheric measurements

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Detailed Terms
Nitrogen trifluoride global emissions estimated from updated atmospheric measurements

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Nitrogen trifluoride (NF₃) has potential to make a growing contribution to the Earth’s radiative budget; however, our understanding of its atmospheric burden and emission rates has been limited. Based on a revision of our previous calibration and using an expanded set of atmospheric measurements together with an atmospheric model and inverse method, we estimate that the global emissions of NF₃ in 2011 were 1.18 ± 0.21 Gg yr⁻¹, or ∼20 Tg CO₂-eq yr⁻¹ (carbon dioxide equivalent emissions based on a 100-y global warming potential of 16,600 for NF₃). The 2011 global mean tropospheric dry air mole fraction was 0.86 ± 0.04 parts per trillion, resulting from an average emissions growth rate of 0.09 Gg yr⁻² over the prior decade. In terms of CO₂ equivalents, current NF₃ emissions represent between 17% and 36% of the emissions of other long-lived fluorinated compounds from electronics manufacture. We also estimate that the emissions benefit of using NF₃ over hexafluoroethane (C₂F₆) in electronics manufacture is significant—emissions of between 53 and 220 Tg CO₂-eq yr⁻¹ were avoided during 2011. Despite these savings, total NF₃ emissions, currently ∼10% of production, are still significantly larger than expected assuming global implementation of ideal industrial practices. As such, there is a continuing need for improvements in NF₃ emissions reduction strategies to keep pace with its increasing use and to slow its rising contribution to anthropogenic climate forcing.

atmospheric composition | climate change | radiative forcing

Alongside the control of carbon dioxide (CO₂), there are significant climate benefits to be gained from limiting emissions of non-CO₂ long-lived greenhouse gases (GHGs) (1). Nitrogen trifluoride (NF₃) has a global warming potential on a 100-y time scale (GWP₁₀₀) of ∼16,600 (see discussion below), and its use has grown rapidly in the manufacture of modern electronic devices (2). The potential for significant NF₃ emissions was only recently recognized (3), and was not considered in the first commitment period of the Kyoto Protocol (4). Despite NF₃’s recent rising importance, difficulties in making atmospheric measurements have prevented a thorough analysis of its global abundance and emission rates (5, 6).

Nitrogen trifluoride’s radiative efficiency of 0.211 W m⁻² ppb⁻¹ is comparable to many anthropogenic GHGs (7); however, its large potential impact on climate arises from its atmospheric lifetime, which is long on societal timescales. Prather and Hsu (3) calculated a lifetime of 550 y (resulting in a GWP₁₀₀ of 16,800); however, three separate kinetic studies have recently suggested a larger sink for NF₃ by reaction with O(¹D) in the stratosphere (8-10). Dillon et al. (9) suggested a revised lifetime of 490 y, yielding the GWP₁₀₀ value of 16,600 we use here.

Use of NF₃ began in the 1960s and 1970s in specialty applications, e.g., as a rocket fuel oxidizer and as a fluorine donor for chemical lasers (11). More recently, beginning in the late 1990s, NF₃ has been used by the electronics industry in the manufacture of semiconductor (SC), photovoltaic cell, and flat-panel display devices (from here on all three are termed SC+). Nitrogen trifluoride can be broken down into reactive fluorne (F) radicals and ions, which are used to remove the remaining silicon-containing contaminants in process chambers (12, 13). The physical and chemical properties of NF₃ make it a safe gas to transport; it is stable and nonflammable, and faster cleaning rates and increased chamber life make it preferable to the perfluorocarbons (PFCs) previously used, primarily hexafluoroethane (C₂F₆, PFC-116). Nitrogen trifluoride was also chosen because of its promise as an environmentally friendly alternative, with conversion efficiencies (to create reactive F) of ∼98% of total use, compared with ∼30% for C₂F₆ (13, 14). Thus, its use has likely played an important role in the SC industry’s strategy to meet its voluntary PFC emission reduction commitments—a reduction in total GHG emissions of 10% between 1995 and 2010 (14, 15).

Given that its production is increasing rapidly to meet demand in end use (manufacture of SC+ devices), that it is a substitute for PFCs for which emissions are already regulated, and that the first atmospheric measurements showed a rising atmospheric abundance, NF₃ is now beginning to be included in global and regional climate legislation (16, 17). It is therefore important to study the atmospheric trend in NF₃ alongside other GHGs in order to provide information that can help evaluate the success of efforts to quantify and regulate its emissions (18).

In this work we supplement and extend the only published atmospheric NF₃ record using a revised primary calibration and an automated measurement technique (5, 6). By combining our measurements with independent industrial production and emission data, we provide optimally derived global emission estimates from 1978 to 2011 using an atmospheric model and an inverse method. We discuss the significance of these emissions and estimate how successful the use of NF₃ has been with respect to its impact on Earth’s radiative budget compared with earlier SC+ industry technology.

Results and Discussion

Atmospheric Measurements. We have measured archived air samples from the Northern Hemisphere (NH) and Southern Hemisphere (SH) to complement and compare with the measurements made previously in our laboratory (6). Additionally, we have extended the in situ record of NF₃ in ambient air at Scripps Institution of Oceanography (SIO), La Jolla, CA (32.87°N, 117.25°W), from April 2011 to March 2012, and have analyzed the entire record to estimate average monthly mole fractions representative


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of the well-mixed lower troposphere at that latitude (Fig. 1). La Jolla receives polluted air masses from the surrounding region, so to estimate these average well-mixed mole fractions (that are needed for global emissions calculations) we identified the measurements that were not influenced by pollution by studying the history of the arriving air masses using the NAME (Numerical Atmospheric dispersion Modelling Environment) Lagrangian particle model (19). The reported in situ baseline abundance (dry air mole fraction) over the 12-mo period increased from 0.91 ± 0.05 parts per trillion (ppt) in April 2011 to 0.97 ± 0.03 ppt in March 2012 (error range is given as 1-sigma of the filtered monthly air data). During December, none of the air masses arriving at La Jolla were classified as baseline, consistent with the recording of some of the highest NF₃ mole fractions measured in air to date.

Fig. 2A shows the atmospheric NF₃ archive measurements made to date and the average baseline monthly mole fractions calculated from the 2011 in situ measurement data from La Jolla. The full set of archived air measurements is also documented in Table S1. Measurements of archived air tanks filled before 1975 and air entrapped in ancient ice collected from Taylor Glacier, Antarctica, found undetectable levels of NF₃, and we conclude that preindustrial NF₃ levels were no greater than 0.008 ppt.

**Global Emissions and Atmospheric Burden.** We used an inverse method to estimate emissions, using a 12-box atmospheric chemistry transport model to couple the sensitivity of semihemispheric mole fractions to global emissions (20). The emissions calculated by the inversion were then used as input into the model, and the monthly mole fraction output and growth rate for the two semihemispheres are plotted alongside the atmospheric measurements in Fig. 2, with annual average mole fractions and growth rates summarized in Table 1. The inversion-derived emissions were able to reconstruct the atmospheric history within uncertainty for the majority of measurements (Fig. S1).

The onset of significant emissions is evident at the beginning of the 1990s, followed by an approximately linear increase through that decade (Fig. 3A). This finding is consistent with the beginning of NF₃ use in the SC industry in the early 1990s. A significant increase in the emissions rate begins at the start of the 2000s with annual emissions increasing roughly linearly at a rate of ~0.09 Gg yr⁻¹ between 1999 and 2011, reaching 1.18 ± 0.21 Gg yr⁻¹ in 2011. The emissions reported in our previous study (6), and corrected for the revised primary calibration (5), were ~0.70 and ~0.77 Gg yr⁻¹ in 2006 and 2008, respectively. In this work we calculate emissions of 0.83 ± 0.19 Gg yr⁻¹ in 2006 (~18% higher) and 1.01 ± 0.19 Gg yr⁻¹ in 2008 (~30% higher). The significantly larger emissions we now calculate are due to an increased number of measurements, a longer data record, and the improved modeling and emissions calculations.

The growth in the average global atmospheric mole fraction from near the detection limit (0.02 ppt) in 1980 to 0.86 ppt in 2011 is the result of a continuous increase in the growth rate to almost 0.1 ppt yr⁻¹ over the past two decades (Fig. 2B). The largest increase in the growth rate occurred between 2000 and 2006, when there was a significant relative rise in NF₃ production and use (2, 23). Using a radiative efficiency of 0.211 W·m⁻²·ppb⁻¹ from Robson et al. (7), an average instantaneous radiative forcing in 2011 is calculated at 1.8 × 10⁻² W·m⁻². Thus, NF₃ is currently contributing ~0.010% of the radiative forcing due to rising CO₂ concentrations since 1750, and 0.017% of the forcing due to non-CO₂ GHGs (1, 26).

**Significance of Current NF₃ Emission Levels.** Although the instantaneous radiative forcing due to NF₃ is currently small, its atmospheric lifetime essentially makes emissions cumulative.
with an effect lasting beyond usual societal timescales. We calculate a revised GWP_{100} of NF_3 of 16,600 using the lifetime calculated by Dillon et al. (9), and use this to calculate CO_2-equivalent (CO_2-eq) emissions (Fig. 3A). Emissions of NF_3 in 2011 were 19.6 ± 3.5 Tg CO_2-eq yr^{-1}, equating to 0.06% of the CO_2 emissions due to fossil fuel combustion and cement production (~34,000 Tg yr^{-1}) in terms of the contribution to radiative forcing over the following 100 y (27).

The SC+ industry uses a suite of fluorinated gases for a range of highly specialized tasks, although the effective mix varies widely between countries and companies (14). Thus, accurately quantifying emissions using “bottom-up” methods (from inventories, i.e., independent of atmospheric measurements) is difficult, and “top-down” methods (dependent on atmospheric measurements) presently only allow us to quantify emissions integrated globally over all industries. Using a combination of top-down and bottom-up data, we have attempted to compare the recent CO_2-eq emissions of NF_3 with those of other more widely studied fluorinated GHGs (Table 2).

The recent emissions of NF_3 (in CO_2-eq), which are almost entirely from production and end use in SC+ manufacture, are larger than those of the other fluorinated compounds from SC+ manufacture, except for CF_4 and possibly C_2F_6. Estimating emissions of CF_4 and C_2F_6 from SC+ manufacture is very difficult because these gases are also emitted during primary aluminum (Al) manufacture (28). Assuming that the bottom-up estimates for CF_4 and C_2F_6 from SC+ and Al industries are underestimated [Mühle et al. (29) showed that the bottom-up estimates from either SC+ or Al manufacture, or both, were too low], for the lower SC+ emissions bound we used the emissions fraction SC+/total from the Emissions Database for Global Atmospheric Research (EDGAR) v4.2 database multiplied by the most recent global estimates from atmospheric studies (25, 29). For the upper SC+ emissions bound we subtracted the bottom-up estimates from Al manufacture from the top-down global total estimates (28, 29). Given that global emissions for C_2F_6 have stabilized and the fact that NF_3 is continuing to replace C_2F_6 (2, 29), it is likely that CO_2-eq emissions of NF_3 already, or will in the near future, exceed those of C_2F_6 from SC+ manufacture.

Emissions of NF_3 in 2010 accounted for between 17% and 36% of emissions (in CO_2-eq) of the most widely used and emitted fluorinated compounds from the SC+ industry, up from between 13% and 28% in 2005 (Table 2). As well as considering the pace at which NF_3 replaces other fluorinated gases, the rise in future NF_3 emissions depends on the SC+ market (likely to grow significantly) and on progress in reducing the amount released. The global NF_3 production rates are not well documented, and estimates have been revised over successive years (3, 7, 23). The latest production estimate from industry is ~12 Gg in 2011 (2); however, an independent report suggests sales are closer to ~10.5 Gg (24). Using a 2011 production estimate of 12 Gg, and scaling emissions in previous years using the relative year-to-year changes documented in more detailed sources (23, 24), we calculate an emissions/production ratio of over 0.20 for the early 2000s, decreasing to 0.10 ± 0.03 in 2011 (Fig. 3B).

These emissions/production ratios (calculated from top-down emissions estimates) can be compared with industry estimates from NF_3 production and different types of end use facilities

### Table 1. Average global tropospheric NF_3 dry air mole fractions (x), mole fraction growth rates (dx/dt), and global emissions flux (F) with associated 1-σ uncertainties

<table>
<thead>
<tr>
<th>Year</th>
<th>x, ppt</th>
<th>dx/dt, ppt yr^{-1}</th>
<th>F, Gg yr^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980</td>
<td>0.020 ± 0.021</td>
<td>0.000 ± 0.006</td>
<td>0.00 ± 0.14</td>
</tr>
<tr>
<td>1985</td>
<td>0.021 ± 0.023</td>
<td>0.001 ± 0.006</td>
<td>0.01 ± 0.13</td>
</tr>
<tr>
<td>1990</td>
<td>0.037 ± 0.026</td>
<td>0.006 ± 0.006</td>
<td>0.07 ± 0.13</td>
</tr>
<tr>
<td>1995</td>
<td>0.080 ± 0.029</td>
<td>0.012 ± 0.006</td>
<td>0.15 ± 0.14</td>
</tr>
<tr>
<td>1998</td>
<td>0.124 ± 0.030</td>
<td>0.018 ± 0.006</td>
<td>0.21 ± 0.15</td>
</tr>
<tr>
<td>2000</td>
<td>0.164 ± 0.031</td>
<td>0.022 ± 0.006</td>
<td>0.27 ± 0.15</td>
</tr>
<tr>
<td>2001</td>
<td>0.189 ± 0.031</td>
<td>0.028 ± 0.007</td>
<td>0.32 ± 0.16</td>
</tr>
<tr>
<td>2002</td>
<td>0.221 ± 0.032</td>
<td>0.037 ± 0.007</td>
<td>0.44 ± 0.17</td>
</tr>
<tr>
<td>2003</td>
<td>0.263 ± 0.033</td>
<td>0.045 ± 0.008</td>
<td>0.54 ± 0.18</td>
</tr>
<tr>
<td>2004</td>
<td>0.312 ± 0.034</td>
<td>0.054 ± 0.008</td>
<td>0.64 ± 0.19</td>
</tr>
<tr>
<td>2005</td>
<td>0.370 ± 0.034</td>
<td>0.062 ± 0.008</td>
<td>0.74 ± 0.19</td>
</tr>
<tr>
<td>2006</td>
<td>0.436 ± 0.035</td>
<td>0.069 ± 0.008</td>
<td>0.83 ± 0.19</td>
</tr>
<tr>
<td>2007</td>
<td>0.508 ± 0.036</td>
<td>0.076 ± 0.008</td>
<td>0.92 ± 0.19</td>
</tr>
<tr>
<td>2008</td>
<td>0.588 ± 0.037</td>
<td>0.083 ± 0.008</td>
<td>1.01 ± 0.19</td>
</tr>
<tr>
<td>2009</td>
<td>0.673 ± 0.038</td>
<td>0.087 ± 0.008</td>
<td>1.07 ± 0.19</td>
</tr>
<tr>
<td>2010</td>
<td>0.762 ± 0.039</td>
<td>0.091 ± 0.009</td>
<td>1.11 ± 0.20</td>
</tr>
<tr>
<td>2011</td>
<td>0.855 ± 0.039</td>
<td>0.095 ± 0.009</td>
<td>1.18 ± 0.21</td>
</tr>
</tbody>
</table>

For comparison with other relevant species, see table 2.1 in ref. 21, chap. 2 and table S1-1 in ref. 22, chap. 1.

### Fig. 3. (A) Top-down NF_3 emissions estimated optimally using the atmospheric measurements and independent emission growth rates as constraints. The a priori emissions used to calculate the emissions growth rates for the inversion were estimated using data from independent sources (2, 14, 23, 24). The EDGAR v4.2 emission estimates are also shown (25). The gray shading represents the ± 1-σ uncertainty of the top-down emissions estimate. CO_2-eq emissions were calculated using a 100-y global warming potential of 16,600 (right axis). (B) The ratio of (top-down) emissions to production illustrates the improved efficiency of processes during production and/or end use over time. The gray shading represents the ±1-σ uncertainty of this ratio considering uncertainty in the top-down emissions estimate and global production.
facilities are typically characterized by the size of emissions. By 7,390, changed total emissions of PFCs from SC−

Table 2. Global emissions of the main greenhouse gases used in semiconductor, photovoltaic cell and flat-panel display manufacture (together termed SC+)

<table>
<thead>
<tr>
<th>Gas</th>
<th>From all sources, Tg CO2-equiv y−1</th>
<th>From leakage during production and SC+ manufacture, Tg CO2-equiv y−1*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF3 (this work)</td>
<td>12.3 ± 3.1</td>
<td>12.3 ± 3.1</td>
</tr>
<tr>
<td>CF3F (29)</td>
<td>77</td>
<td>6−46</td>
</tr>
<tr>
<td>C2F6 (29)</td>
<td>30</td>
<td>16−25</td>
</tr>
<tr>
<td>SF6 (30–32)</td>
<td>140</td>
<td>6–11</td>
</tr>
<tr>
<td>CHF3 (33)</td>
<td>180</td>
<td>0.9</td>
</tr>
<tr>
<td>C2F4F2 (34, 35)</td>
<td>5–10</td>
<td>6–11</td>
</tr>
</tbody>
</table>

100-y GWPs used to calculate CO2-equiv emissions: NF3 16,600, CF3 7,390, C2F6 12,200, SF6 22,800, CHF3 14,800, and C2F4F2 10,300. Uncertainties are given at the 1-s level for NF3; otherwise ±20% (1-s) should be assumed, and very poorly constrained emissions are given with a range.

*Calculated from a combination of the top-down global emission estimates and the ratios of emissions from SC+ to the global totals calculated from EDGAR v4.2 (25). The upper bounds for the CF3 and C2F6 used emission estimates from the production of primary aluminum (28) subtracted from the top-down emissions (29).

From 2008 (for CF3 and C2F6) and 2009 (for CHF3) emission estimates.

...to infer the possible global levels of abatement that might have occurred. We therefore considered two cases at the extreme ends of possible abatement levels (Fig. 4). In scenario 1 we considered zero abatement, i.e., that NF3 has not been abated and if C2F6 had been used it would not have been abated. Under this scenario we calculated a maximum emissions saving of 220 Tg CO2-equiv y−1 in 2011. However, this finding is likely an overestimate because we know that abatement in some facilities does occur for NF3 and would have occurred for C2F6, with with increasing abatement the emissions benefit from using NF3 over C2F6 decreases. In scenario 2 we assumed a 98% abatement efficiency for C2F6 and NF3 in new facilities, and from this we estimated a minimum emissions saving of 53 Tg CO2-equiv y−1 in 2011. However, this finding is likely to be an underestimate because we expect that not all modern facilities would have been abating optimally, and with lower abatement levels the emissions benefit from using NF3 over C2F6 increases. A third scenario is plotted in Fig. 4 to show the negative emissions saving had C2F6 been completely destroyed during end use; this serves to illustrate how large the estimated emissions savings in scenarios 1 and 2 are relative to actual current emissions of NF3. Although it is not possible to further constrain the avoided emissions, our analysis shows that the shift from C2F6 to NF3 has been significantly beneficial in terms of reducing the total CO2-equiv impact of SC+ industry PFC emissions over the past decade.

Conclusions

Our expanded data set and revised primary calibration show that the global atmospheric abundance of NF3, a potent anthropogenic GHG, continues to rise, reaching a mean concentration in the global background troposphere of 0.86 ± 0.04 ppt during mid-2011, and that its annual emission rate has risen throughout the past decade to ∼1.2 Gg y−1 in 2011. Thorough bottom-up
estimates of emission rates are lacking because requirements for reporting are only now being initiated in legislation. Nonetheless, from our analysis of the available independent information sources, it is clear that bottom-up emissions are currently being significantly underestimated on a global scale.

Given the available information on production rates, we calculated that the ratio of emissions to production has decreased significantly since the introduction of NF₃ in SCF- manufacturing, probably because of efficiency gains in manufacturing and end use, and a shift toward semiconductor production in more modern facilities that use NF₃ with very high efficiency (∼98%). Our integrated global analysis therefore probably masks significant variability in emissions performance across the globe and among industrial sectors, which makes estimating the emissions saving over use of C₂F₆ challenging and uncertain. Nonetheless, our analysis suggests that the savings in recent years from the shift to NF₃ are substantial.

Continued efforts are needed to increase the utilization efficiency during application and to minimize emissions in production so that the full climate benefit of NF₃ use can be realized. This shift will become progressively more important as the demand for NF₃ rises significantly over the coming years. Together with voluntary and legislative action to curb emissions of NF₃, bottom-up inventories will need improving, alongside atmospheric monitoring and modeling work to provide independent emissions verification, especially on regional and national scales.

Materials and Methods

Instrumentation and Measurement Method. We have adapted a Medusa preconcentration GC/MS system to make automated measurements of NF₃ at SIO (5, 36). The measurement cycle lasts 65 min, and each sample is bracketed by analyses of a compressed reference gas, resulting in a calibrated ambient air measurement every 130 min (5). For archive samples, at least three separate measurements were made, and the measurement error was evaluated as 1 σ of the three measurements.

The measured archived air samples include NH samples collected at La Jolla from 1973 to 1991 and at the Trinidad Head, CA, Advanced Global Atmospheric Sciences Experiment (AGASE) station (41.05°N, 124.15°W) from 1998 to 2010, and SH samples from the Cape Grim Air Archive collected at the Baseline Air Pollution Station at Cape Grim, Tasmania (40.68°S, 144.69°E) (37). The ice core samples were collected in the 2011–2012 field season at Taylor Glacier, Antarctica, and the air was extracted on-site using previously described methods (38, 39). The air samples had ages of ∼11,360 B.P. (Preboreal), ∼11,500 B.P. (transition from Preboreal to Younger Dryas), and ∼11,600 B.P. (Younger Dryas; B.P. relative to 1950 A.D.). We found undetectable levels of NF₃ in 2-L samples of these extractions. To further constrain the preindustrial global abundance below the routine detection limit, we preconcentrated and measured 6 L of air from one Preboreal age sample.

Calibration. We report NF₃ concentrations on an updated calibration scale, SIO-12, the preparation of which is described by Arnold et al. (5). This scale is based on four primary gravimetric standards prepared in a whole-air matrix to minimize the risk of bias due to interference with other atmospheric constituents; its estimated overall uncertainty is 2%. For our 2008 measurements we used a preliminary volumetric calibration scale that was prepared using a digital quartz pressure gauge and a fixed volume to add ∼3 ppt of NF₃ from a volumetric NF₃/N₂O mixture to a large aliquot of whole air (5). At the time we recorded a small −0.597 torr zero offset in the Paroscientific 2300 torr full-scale pressure gauge but failed to apply that offset to the unusually small 2.183 torr pressure measurement associated with the required very small aliquot of NF₃. As a result, we underreported the amount of NF₃ added to the 2008 standard by 21.5%, and thus underestimated the amount of NF₃ in the atmosphere by this same percentage. The 2008 preliminary standard has now been measured directly against the SIO-12 gravimetric scale (4), the results of which show the 2008 numbers to be 19.9% too low. The revised gravimetric standard thus agrees with the zero-offset corrected 2008 volumetric standard within the expected ∼3% combined uncertainty of the two methods (5, 6). Accordingly, the NF₃ measurements reported by Weiss et al. (6) that are also used in the present work have been corrected to the gravimetric scale. It must also be stressed that, except for the initial SIO-2008 NF₃ scale, all SIO calibration scales used for atmospheric trace gas measurements in the AGAGE program are entirely gravimetric and are not vulnerable to such pressure measurement uncertainties (40).

Pollution Analysis of In Situ Measurements. The NAME model was run in backward mode using UK Met Office global resolution meteorology (∼25 km). Tracer particles were released at the sampling site over every 3-h period, and the 19-d back trajectory histories of these particles were estimated. In a similar method described by Manning et al. (19) for calculating methane and nitrous oxide baseline values at Mace Head, Ireland, threshold criteria were used to classify the air masses arriving at La Jolla for each 3-h period: air arriving via the continent, stagnant local air, or air from equatorial latitudes were classified as nonbaseline.

Global Emissions Calculation: Inverse Method and Atmospheric Chemistry Transport Model. Given that prior emission rate estimates of NF₃ are likely inaccurate, and because our atmospheric measurements are relatively sparse, we used a growth-based Bayesian inverse method to optimally derive global emissions (20). Instead of using absolute emission rates, this method uses the more reliably understood year-to-year growth in emissions. From the total NF₃ bottom-up emissions, discussed above, we calculated the annual emissions rate growth and included this as a constraint in the inversion.

We calculated bottom-up emissions estimates from data that are publicly documented on NF₃ production levels (2, 23, 24), and emission factors that have been estimated or directly measured (14, 23, 41). Fthenakis et al. (23) discuss the reduction in emission factors (emitted/produced) from two of the largest manufacturers of NF₃, Air Products and Kanto Denka. Using this information, we applied emission factors of 10% from the two facilities linearly with respect to time to 7% in 1997, to 5% in 2004, 2% in 2009, and 1% in 2012. Calculating a global bottom-up emissions estimate for end use is very difficult given the different types of technology and different levels of abatement in use (14, 41). We calculated emissions from end use with an emission factor (emitted/generated) of 0.02 for all years, which is in reasonable agreement with the available data in the present work (14, 23). The full time-series is shown in Table S2. The EDGAR v4.2 database published 0.1° longitude × 0.1° latitude gridded annual emissions from 1978 to 2008 (for which the origin of information is not documented) (25); however, it appears that those estimates are unrealistically low based on our bottom-up estimates (Fig. 3A; Table S2).

For the inversion we computed the sensitivity of atmospheric mole fraction and global emissions of NF₃ to errors in the AGAGE 12-bottom-up dataset. The details of the model structure and inversion method are described in SI Materials and Methods. We used a NF₃ lifetime estimated by Dillon et al. (9) of 490 y, which considers reaction with O(³D) and photolysis by UV in the stratosphere, and a negligible reaction with OH radical (3, 8–10, 45, 46). The model was run multiple times with global emissions perturbed individually by 1 Gg in each year. The sensitivity matrix for the inversion was then constructed from these outputs so that each element contained the mole fraction perturbation in a particular model box on a particular month (where data exist) due to emissions in a particular year. Although our box model could allow us to solve for semihemispheric emissions, the low frequency in time and space of atmospheric measurements only allowed for global emissions to be accurately resolved. The spatial distribution of emissions was taken from the annual EDGAR v4.2 gridded emission dataset. These estimates for 1978 with 94% of emissions from 30°–90° latitudes in the NH, and end in 2008 with these latitudes contributing 47% of emissions. Remaining emissions originate from the lower NH latitudes (0°–30°).

The total measurement uncertainty used in the inversion was calculated as the square root of the sum of the following squared errors: errors resulting from sampling frequency, measurement-model mismatch, measurement precision, and scale propagation (see SI Materials and Methods for further details). The inversion was carried out 1,000 times using 1,000 alternative sensitivity matrices and measurement vectors constructed from the randomly perturbed parameters in the model and calibration scale, respectively. The uncertainty associated with the average emissions from the 1,000 inversions was combined with the inherent uncertainty from the inversion (taken from the error covariance matrix) to produce the final 1σ uncertainties.

To estimate the annual average global tropospheric mixing ratios and related uncertainties (Table 1), the model was run 1,000 times using the annual emissions with normal distributions based on the associated uncertainties derived from the inversions. Each run produced mole fraction outputs for the lower troposphere in each of the semihemispheres. The growth rates and associated uncertainties were calculated similarly using the first derivative of each of the 1,000 model outputs fitted with a cubic spline curve.

Emissions-Saving Analysis. The following assumptions were used in this emissions saving analysis. First, emissions of NF₃ during end use only were
calculated by accounting for emissions during production: The upper limit for emissions during production was taken as half the total top-down estimate, and the lower limit was taken from bottom-up estimates of emission factors and production (2, 23, 24). Second, utilization efficiencies were 98% and 70% for NF3 in modern and older end-use facilities, respectively, corresponding to utilization efficiencies of 44% and 30% for CF4, respectively (14). Third, when abatement was considered it was only in modern facilities and assumed 98% for both NF3 and CF4. Fourth, 10% by mass of the CF4 supplied was assumed to be converted into CF2 (14), and an abatement efficiency of 40–80% for this CF2 was assumed in modern facilities (14, 47). And fifth, the production of CF2 from silicon carbide cleaning was small and consistent between methods (14), and was therefore not considered. Further details of the method used to calculate the emissions saving are given in Fig. S1 and SI Materials and Methods.

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