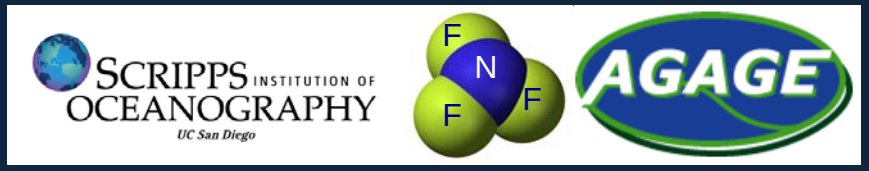

Nitrogen Trifluoride Global Emissions and Emission Factors Estimated from Atmospheric Observations

Tim Arnold [a], Christina Harth [a], Jens Mühle [a], Jooil Kim [a], Peter Salameh [a], Alastair Manning [b], Diane Ivy [c], and Ray Weiss [a]

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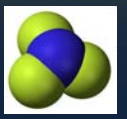
[b] Atmospheric Dispersion Group, UK Met Office, Exeter, UK.

[c] Center for Global Change Science, Department of Earth, Atmospheric, and Planetary Science, Massachusetts Institute of Technology, USA.

Background – atmospheric chemistry



NF_3, the greenhouse gas missing from Kyoto

Michael J. Prather[1] and Juno Hsu[1]

Received 5 May 2008; accepted 27 May 2008; published 26 June 2008.

[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 chemi 1,000 facility

Prather and Hsu, GRL, 2008

- Used a 3D chemical transport model to calculate an atmospheric lifetime as ~550 years (using work of Molina et al., 1995 and Sorokin et al., 1998)
- Calculated a GWP_{100} of 16 800 (using radiative efficiency from Robson et al., 2006)

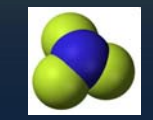
Reactive and nonreactive quenching of $O(^1D)SO_2F_2$, NF_3, and SF_5CF_3

Zhijun Zhao[a,1], Patrick L. Laine[a], J. Michael Nicovich[b], and Paul H. Wine[a,b,2]

Zhao et al., PNAS, 2010

- Faster reaction in the stratosphere with $O(^1D)$, also verified by Dillon et al. (2011) leading to a calculated lifetime of ~480 years
- Calculated a GWP_{100} of 16 600

Background - uses



NF_3 as a replacement for C_2F_6 (PFC-116) in CVD chamber cleaning (part of semiconductor production)

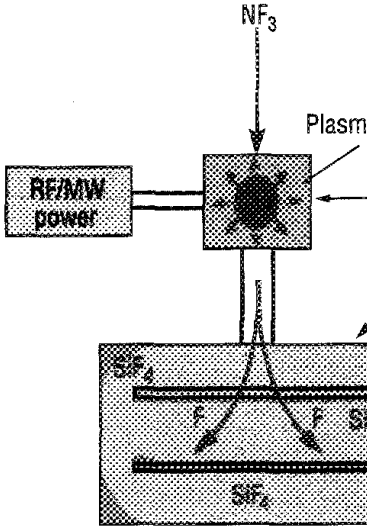


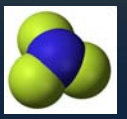
Table 3 Typical MMTCE (per μm deposition) values for CVD chamber cleans*

	Standard C_2F_6	Optimized C_2F_6	Remote NF_3
Applied Materials DxL (TEOS): 200mm [12,15]	34×10^{-9}	5×10^{-9}	0.04×10^{-9}
Applied Materials DxZ (TEOS): 200mm [16–18]	8×10^{-9}	2×10^{-9}	0.04×10^{-9}
Novellus Systems Concept-2 (TEOS): 200mm [7, 8]	8×10^{-9}	N/A**	N/A
Novellus Systems Concept-1(TEOS): 150mm [15]	33×10^{-9}	16×10^{-9}n/a	N/A
Applied Materials [13] Ultima (USG): 200mm	N/A	N/A	0.10×10^{-9}

From Johnson et al., Solid State Technology, 2000

NF_3 demonstrated a huge reduction in CO_2 equivalent emissions compared to C_2F_6 and "*It is accepted that most new CVD equipment will be cleaned using NF_3 chemistry*"

Background – atmospheric monitoring



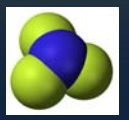
- Atmospheric CF_4 (~80 ppt) is measured with precision of ~0.1% by the "Medusa" GC/MS (Miller et al., 2008)

- Weiss et al. (2008) detected atmospheric NF_3 but they had to go looking for it! Method was extremely consuming in terms of instrument time and personnel time (= expensive).

- 11 samples of air archived from 1977 to 2008 were measured showing NF_3 was growing at a rate of 11% in 2008

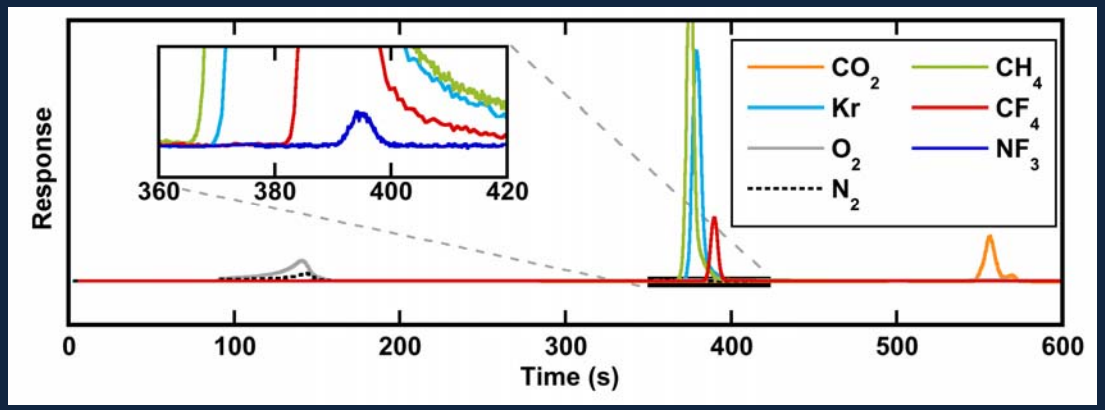
- Important to keep measuring and start monitoring

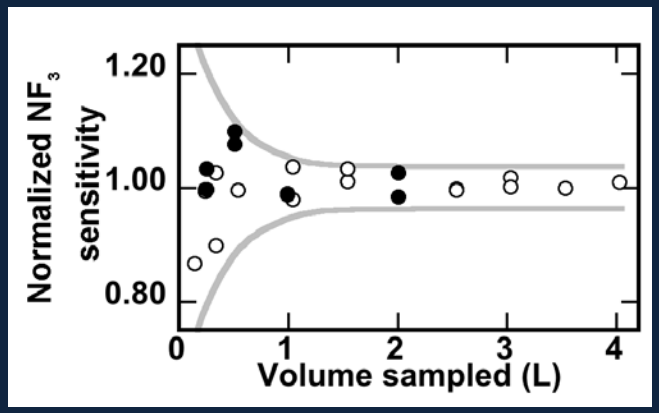
Background – atmospheric monitoring



Problems with measuring NF3:

- Very volatile with b.p. ~-130 C (similar to CF4)
- Low abundance
- Poor sensitivity in the mass spec
- Shows non-linear detection with many (useful) chromatographic materials!

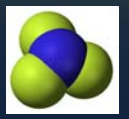




Arnold et al., (in press)

Adapted Medusa GC/MS of Miller et al., *Anal. Chem.* (2008) for measurement of NF_3 alongside all the other halogenated species important for studying greenhouse gases and stratospheric ozone depletion.

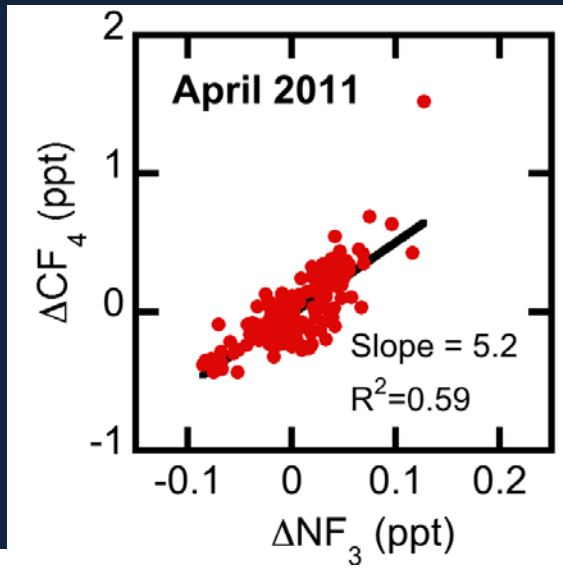
Background - calibration

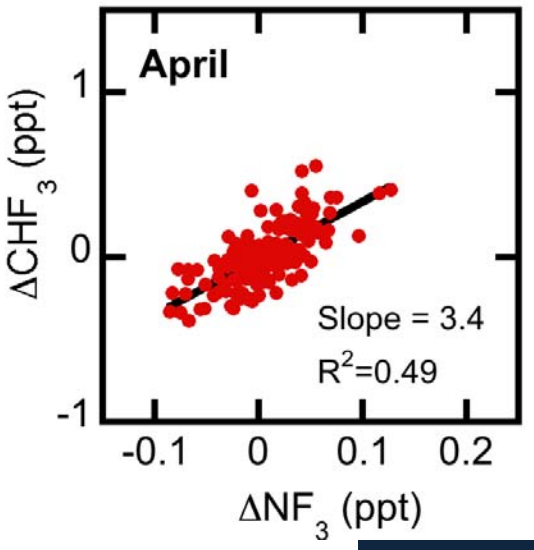


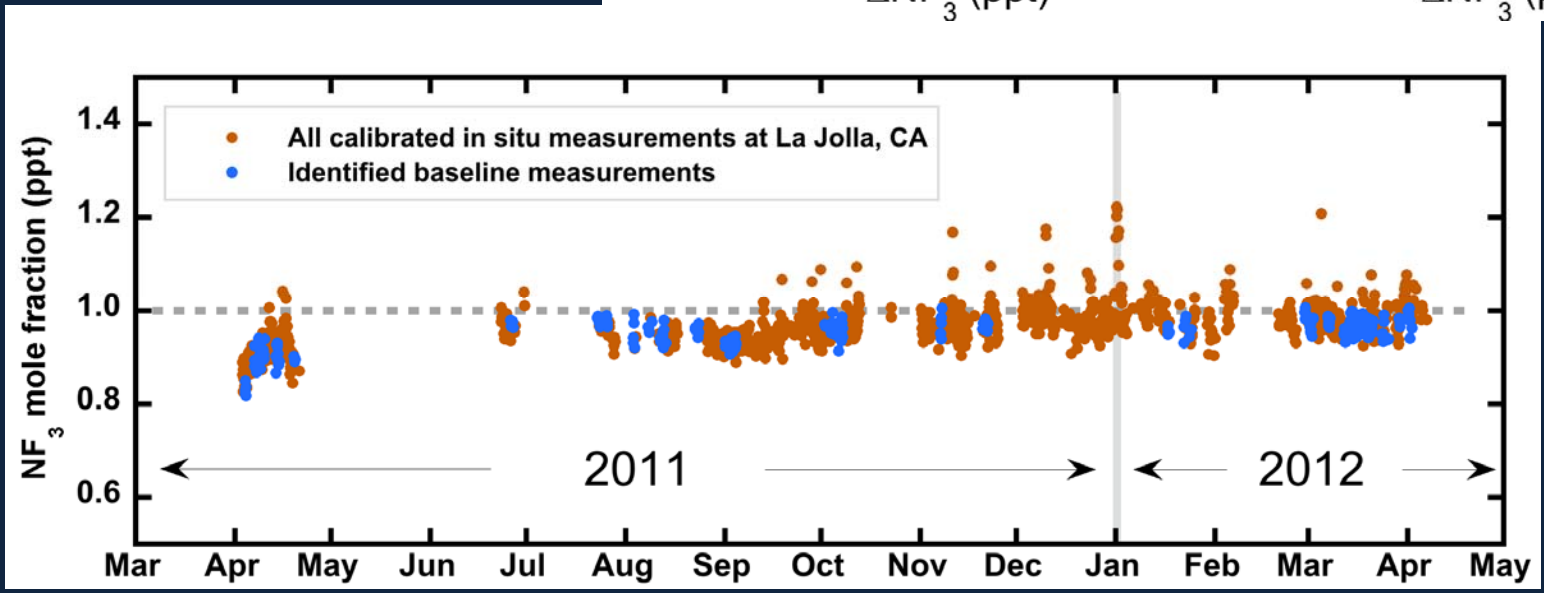
- Four separate gravimetric standards were prepared using a standard addition method to account for matrix related issues during measurement
- Relative standard deviation between prepared standards was 0.51% (with an estimated uncertainty of 2%), however, this calibration calculated the atmospheric mole fraction to be 25% greater that that reported by previously.
- The source of the calibration error in 2008 was identified and corrected for (Arnold et al., in press). The two calibrations now agree within 1.4% (typical 1-σ measurement relative precision is 1.5%)
- Additional confidence in our calibration comes from CF_4, which was included alongside NF_3 as a gas to be calibrated.
- The previous SIO-CF_4 scale (see Mühle et al., 2010) and this new calibration differed by only 0.11% which is insignificant given that typical 1-σ measurement precisions are ~0.1%.

In situ measurements

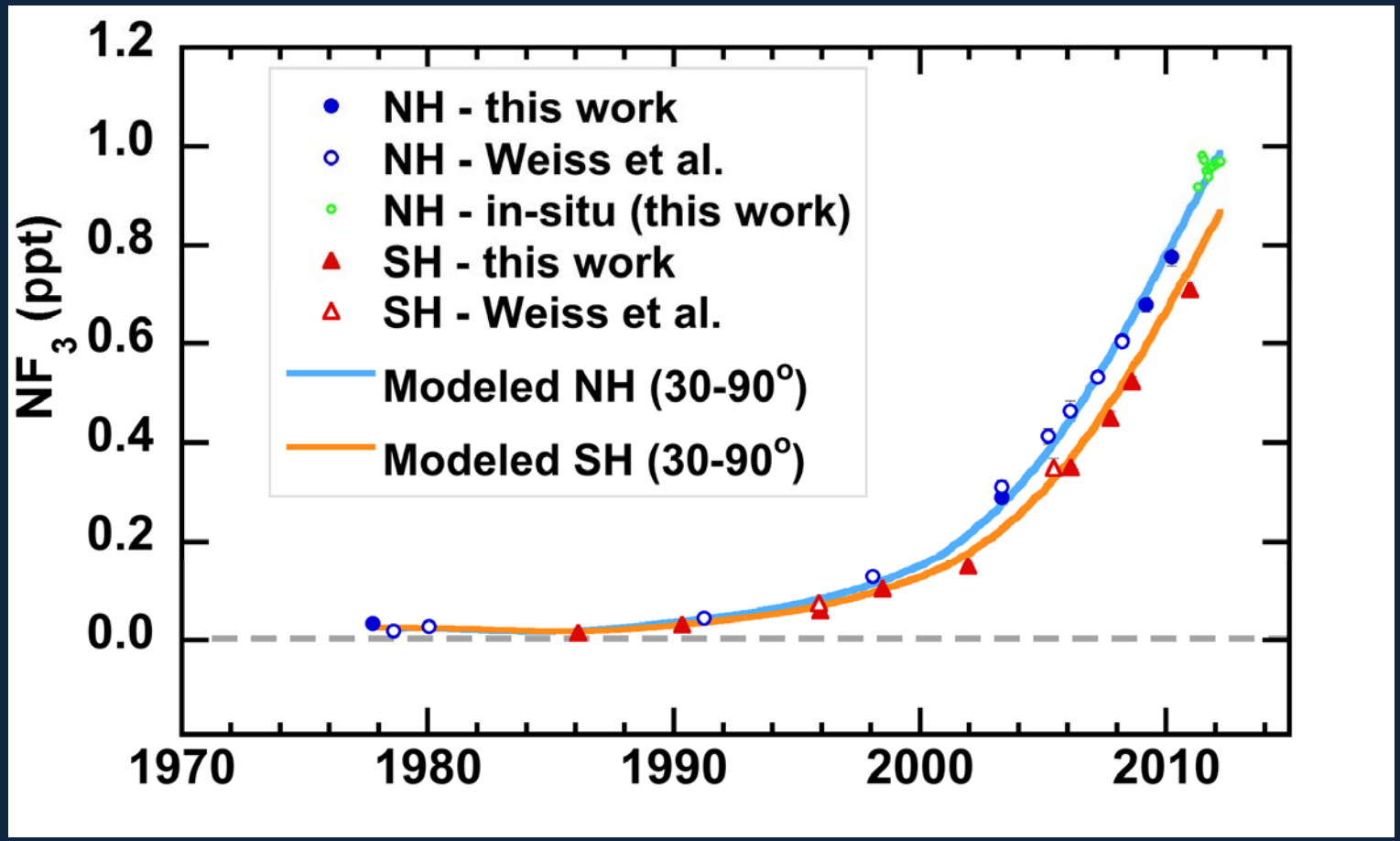
So far… calibrated measurements made at La Jolla, CA from April 2011 to present



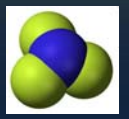




Revised and updated historical record



Bottom-up emission estimates



Supply estimates

Robson et al. (2006) estimated 2.3 kt in 2006
Prather & Hsu (2008) estimated 4 kt for 2008
Fthenakis et al. (2010) estimated 7 kt for 2008 and 4kt for 2006
Maykut & Maroulis pers. comm. (2011) 9.5 kt for 2008

EDGAR v4.2
(Only end-use?)

"7% in 1997, 5% in 2004, and 2% in 2006-2009; they are targeted to decline to 0.5%" *Fthenakis et al. (2010)*

Prior emission estimates

+ atmospheric measurements

Better emissions estimate

"85% are used in processes which release an upper limit of 2% to the atmosphere. The remaining 15% are used in processes which release an estimated 30%" *Robson et al. (2006)*

Top-down emission estimates

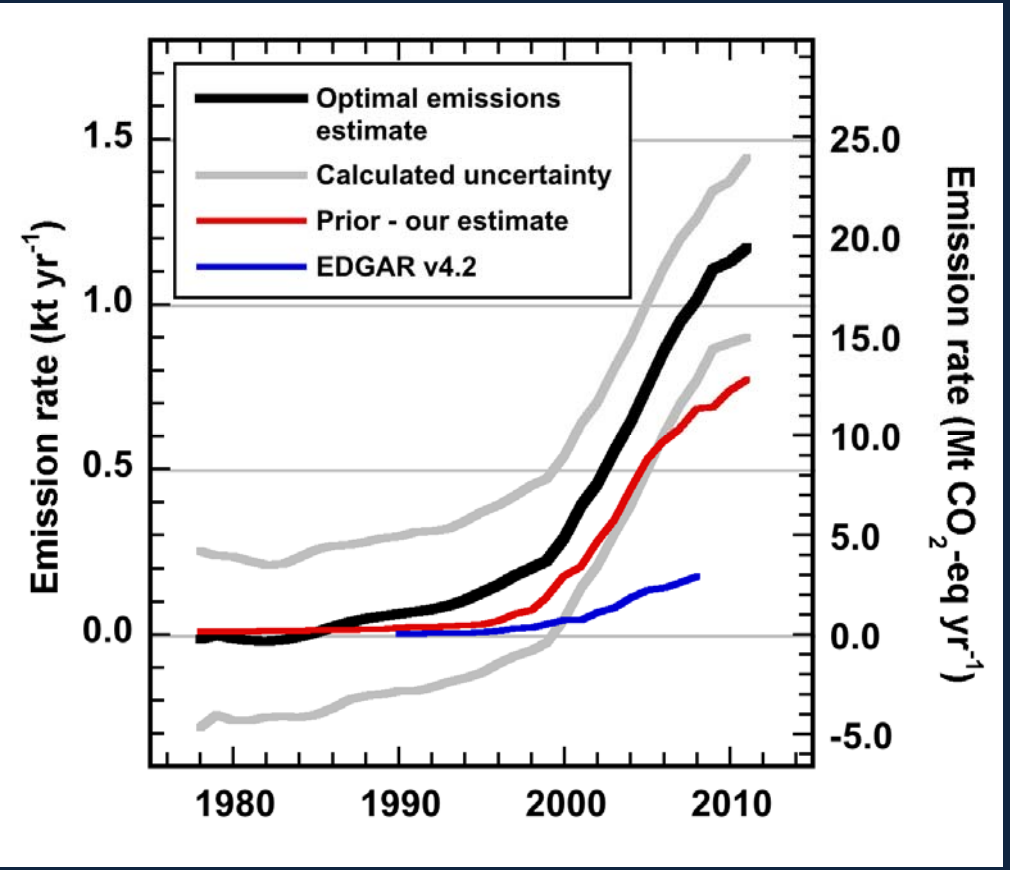
Method

Used 2D atmospheric model (AGAGE 12-box) to calculate the sensitivity of atmospheric mole fractions to changes in emissions

Bayesian inversion based on a prior emissions growth rate estimate (Rigby et al., 2010)

Considered uncertainties in the model parameters, measurement error, measurement-model mismatch, uncertainty in calibration, uncertainty in the prior growth data

Results



Top-down emission estimates

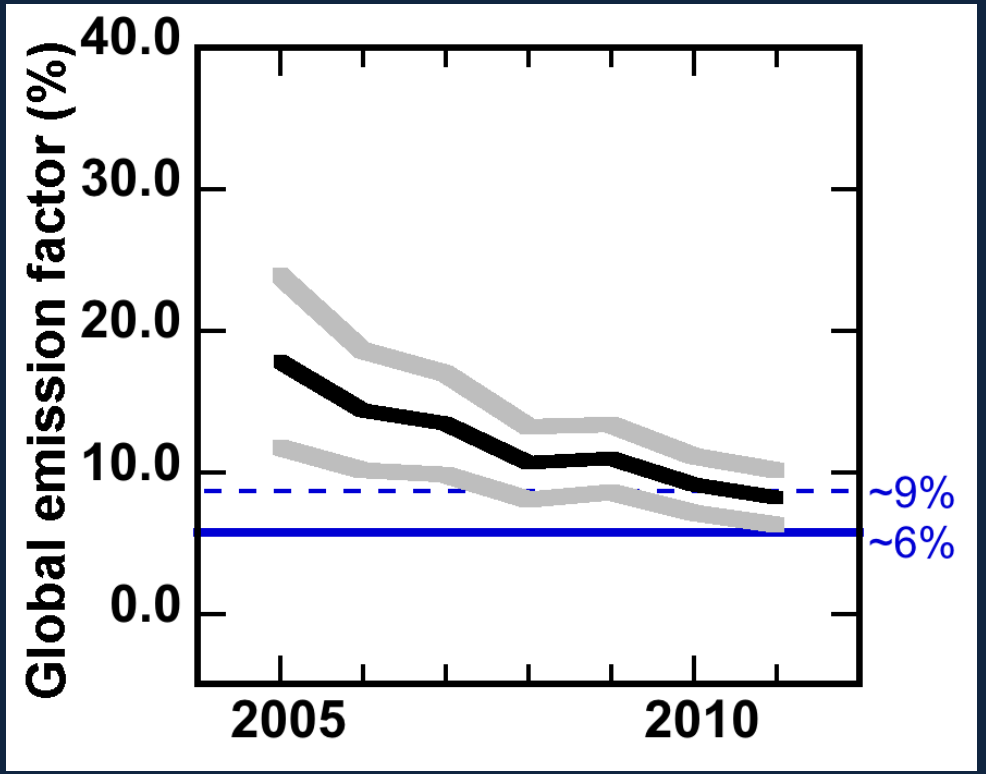
Global emission factors i.e. industry wide integrated

EM = emissions/supply x 100

Air Products suggests that emission factor from production to end-use in 2009 was <2%

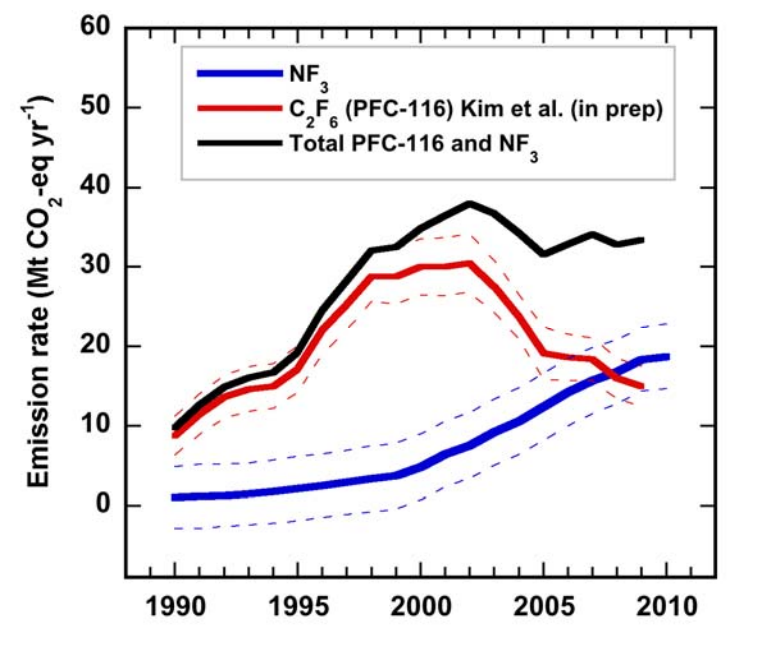
Market share of Air Products was 25%, suggesting the rest of industry had an emission factor of 15%

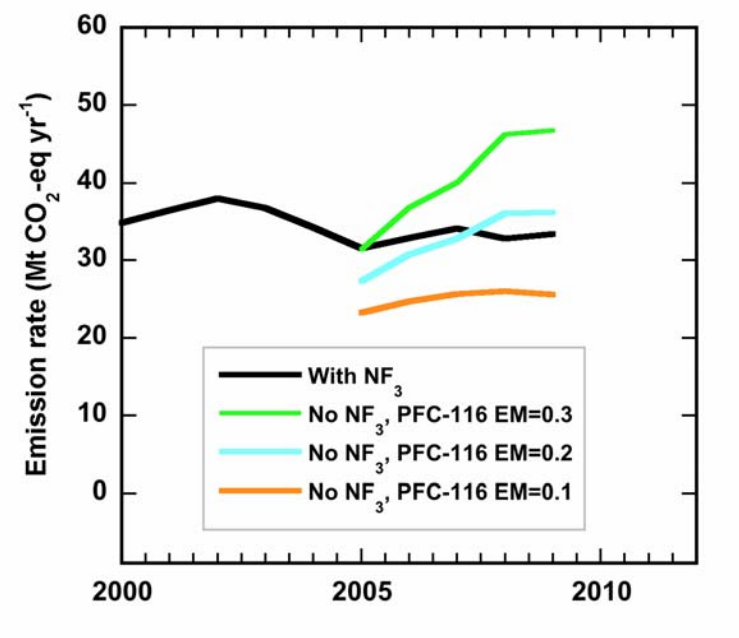
A few clean players let down by some dirty ones? Or is industry estimating a best case scenario?



Top-down emission estimates

NF_3's climate benefit



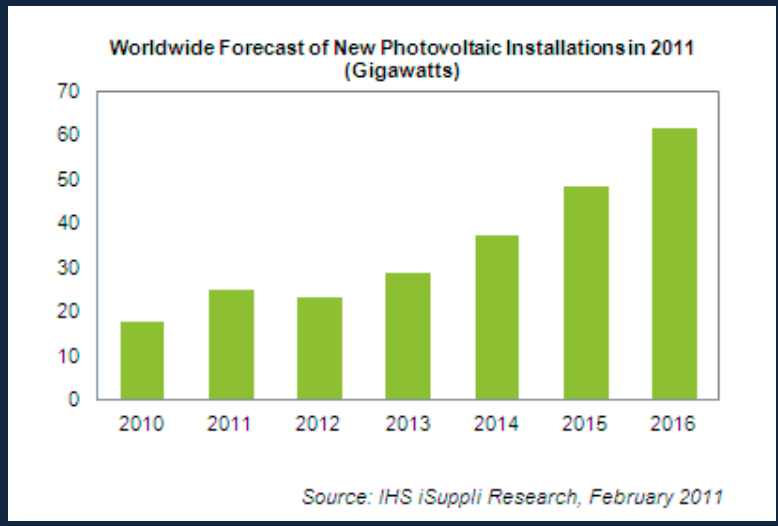


Outlook

NF_3 market

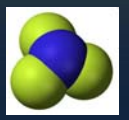
Mccoy, Chemical and Engineering News (2011)

"NF3 is still the design basis for chamber cleaning applications and will be for the foreseeable future"



http://www.isuppli.com/

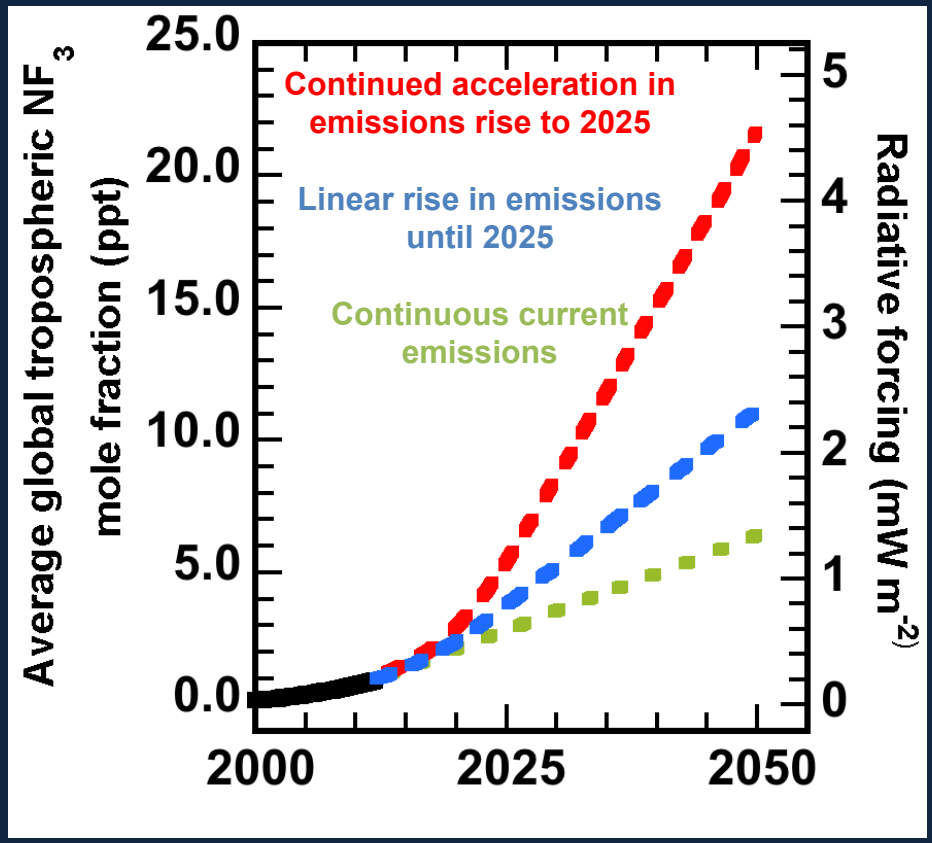
Outlook



Atmospheric NF_3 projections

In 2011 radiative forcing due to NF_3 was 0.01% of that due to the CO_2 rise since preindustrial times

Current emissions of around 1.2 kt (20 Mt CO_2-eq / yr), which is 0.06 % of the most recent estimate of global CO_2 emissions due to fossil fuel combustion and cement production

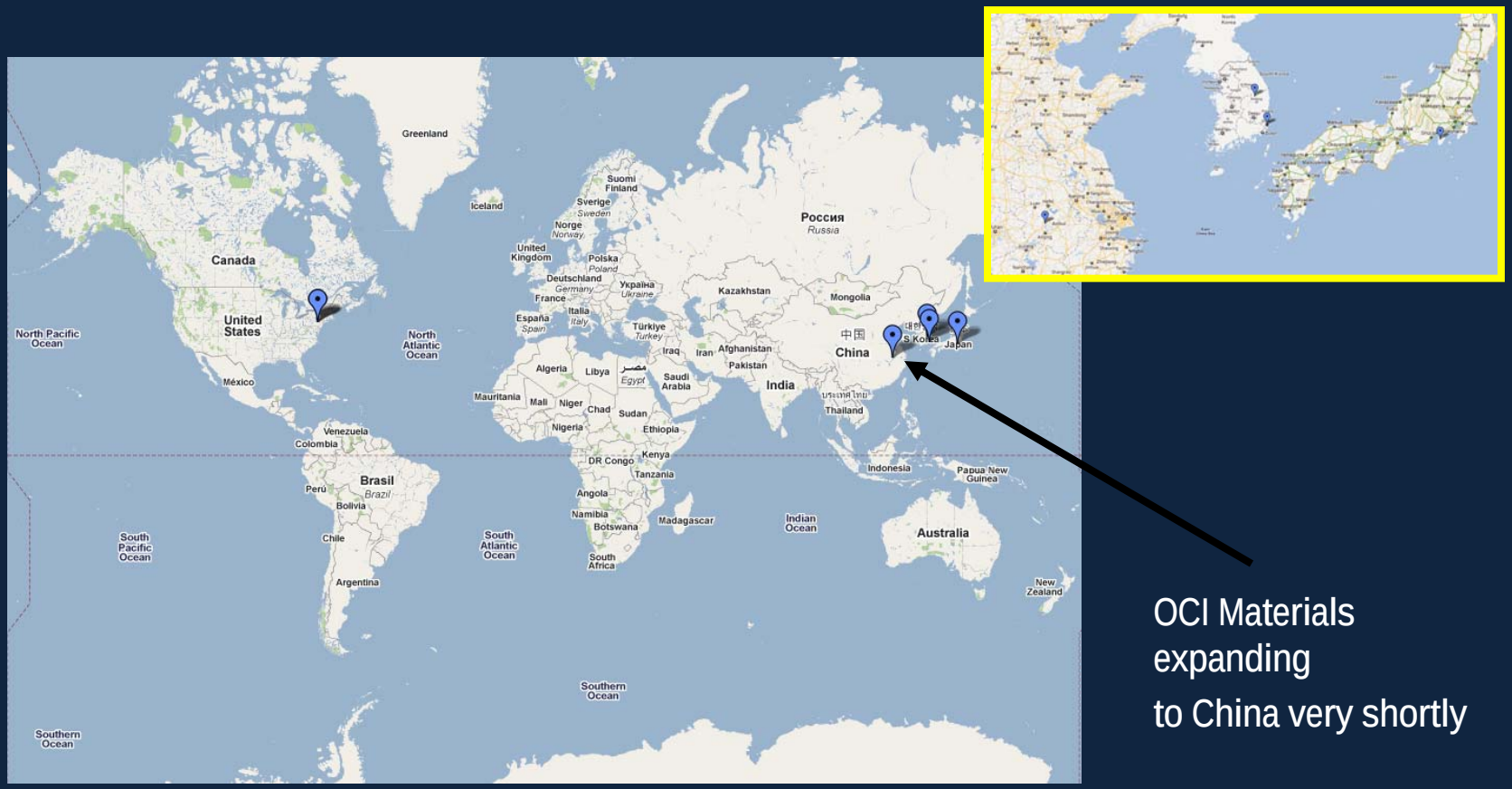


Projected (RCP scenarios) suggest radiative forcing of CO_2 in 2050 to be between 3000 and 5000 Wm^{-2}

Outlook

Atmospheric NF_3 monitoring

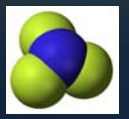
Bulk supplied by three companies: Air Products, OCI Materials and Kanto Denka



OCI Materials expanding

to China very shortly

Summary



- Northern Hemisphere (32.9° N 117.3° W) background NF_3 now at 1 ppt and growing at ~0.1 ppt yr^{-1}
- Global 'top-down' emissions estimated at 1.2 kt in 2011, which equates to nearly 20 Mt CO_2-eq.
- Emissions of NF_3 now probably exceeding C_2F_6 from the electronics industry
- Radiative forcing in 2011 ~0.01% of that due to CO_2
- Emissions in 2011 equate to ~0.06% due to CO_2 (using a 100-yr GWP)
- Data on industry supply estimates suggest an emission factor of ~ 8% which has decreased from 17% in 2005
- We need to start global monitoring

Thanks to…

AGAGE colleagues
Peter Maroulis (Air Products)
John Langan (Air Products)

Upper Atmospheric Research Program of NASA