The surprising case of CFC-11:
Have we fallen off the path to ozone layer recovery?

Steve Montzka
NOAA Global Monitoring Division, Boulder, USA

Sunrise at the Mauna Loa Baseline Observatory

Thanks to:

Colleagues at NOAA and CIRES.

All co-authors on associated papers

Montzka *et al.,* 2018, https://doi.org/10.1038/s41586-018-0106-2

Rigby *et al.,* 2019, https://doi.org/10.1038/s41586-019-1193-4

Ray *et al*., 2020, https://doi.org/10.1038/s41561-019-0507-3

Station personnel and cooperative institutes around the world helping with flask sampling and instrument maintenance

AGAGE community of scientists

The 1987 Montreal Protocol

* Designed to heal the stratospheric ozone layer (limit UV exposure), which showed large depletions particularly over Antarctica during springtime.
* Mandated a global phase-out of production & trade of ozone-depleting gases.
* The first universally ratified treaty in UN history.
* Parties have held 2 meetings/yr since the late 1980s to ensure continued success.

Problem causers: long-lived chlorinated and brominated gases:

e.g., Chemicals used

- in refrigeration & air conditioning, foam-blowing, as solvents (CFCs, or chlorofluorocarbons)
- as chlorinated solvents (CH_3CCl_3, CCl_4)
- in fire-extinguishing (halons-1211,halon-1301)
- as pesticide (methyl bromide)

1st generation substitutes:

HCFCs (hydrochlorofluorocarbons)

2nd generations substitutes:

HFCs (hydrofluorocarbons)

A view of the Meeting of the Parties, Rome, Nov., 2019

Despite a warning over 45 years ago…

Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

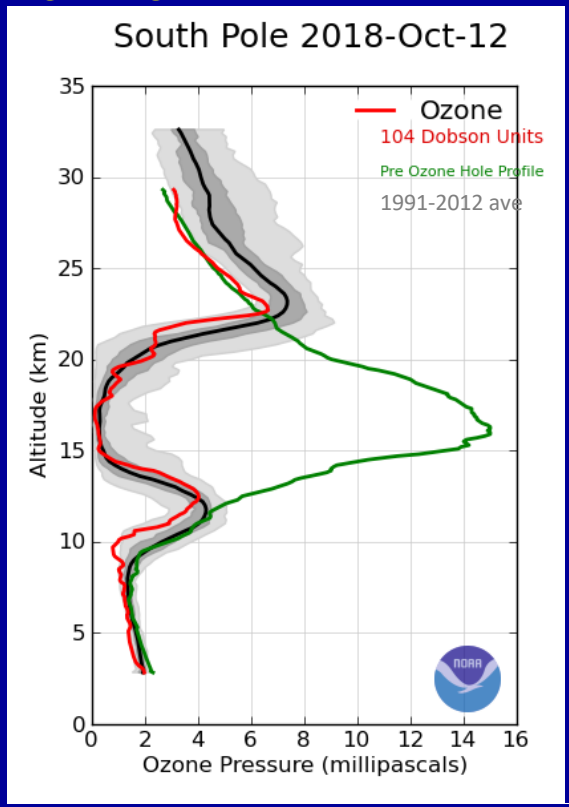
Department of Chemistry, University of California, Irvine, California 92664

Nature, 249, 810, 1974

…and the universal ratification of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987

The stratospheric ozone layer is far from recovered:

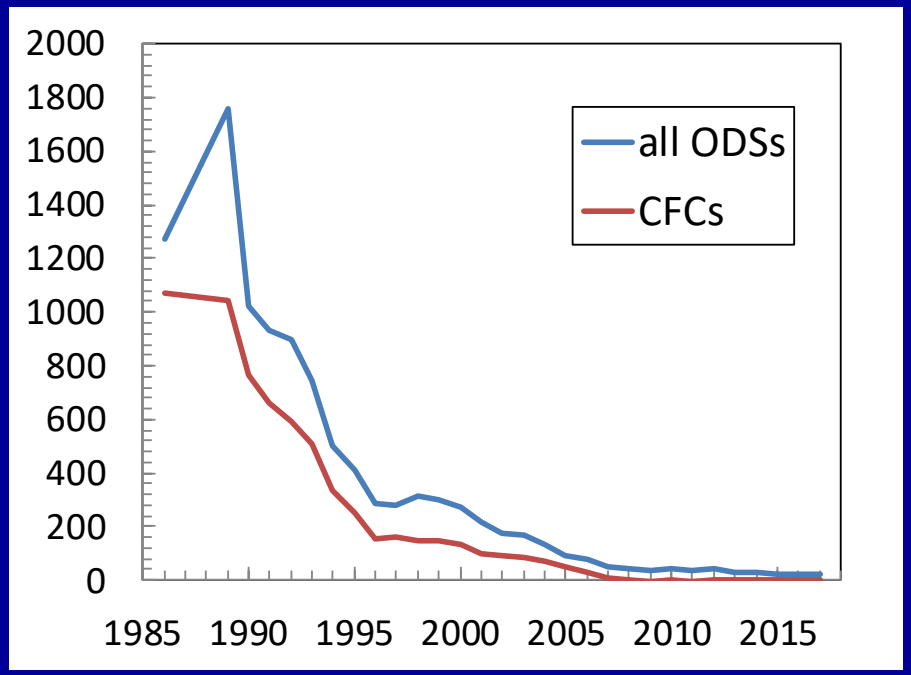
Ozone over South Pole during fall of 2018 (red line) (ozonesonde flights by NOAA-GMD):



So why is the Montreal Protocol considered perhaps the single most successful international agreement ever?

Adherence to the Montreal Protocol has led to:

1) Near elimination of ozone-depleting substance (ODS) production, particularly chlorofluorocarbons (CFCs)



CFC production reportedly phased-out in 2010

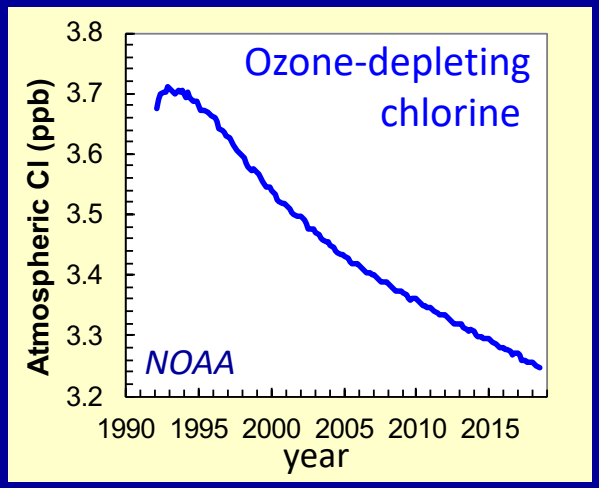
Minimal production reported by 2007

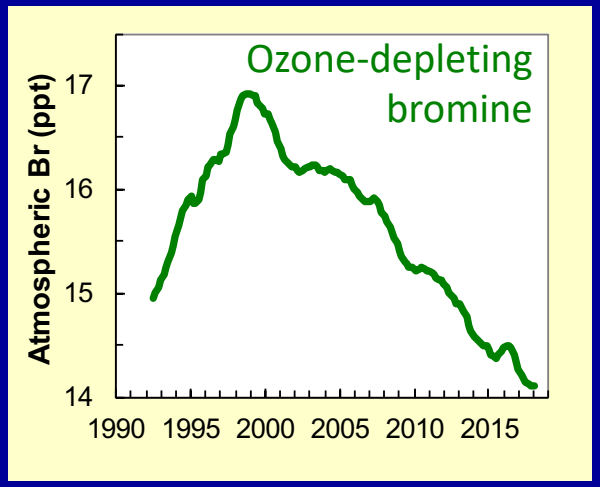
* Reported to the WMO/UNEP Ozone Secretariat

So why is the Montreal Protocol considered perhaps the single most successful international agreement ever?

Adherence to the Montreal Protocol has led to:

1) Near elimination of ozone-depleting substance (ODS) production, particularly chlorofluorocarbons (CFCs)
2) declines in ODS emissions and concentrations:





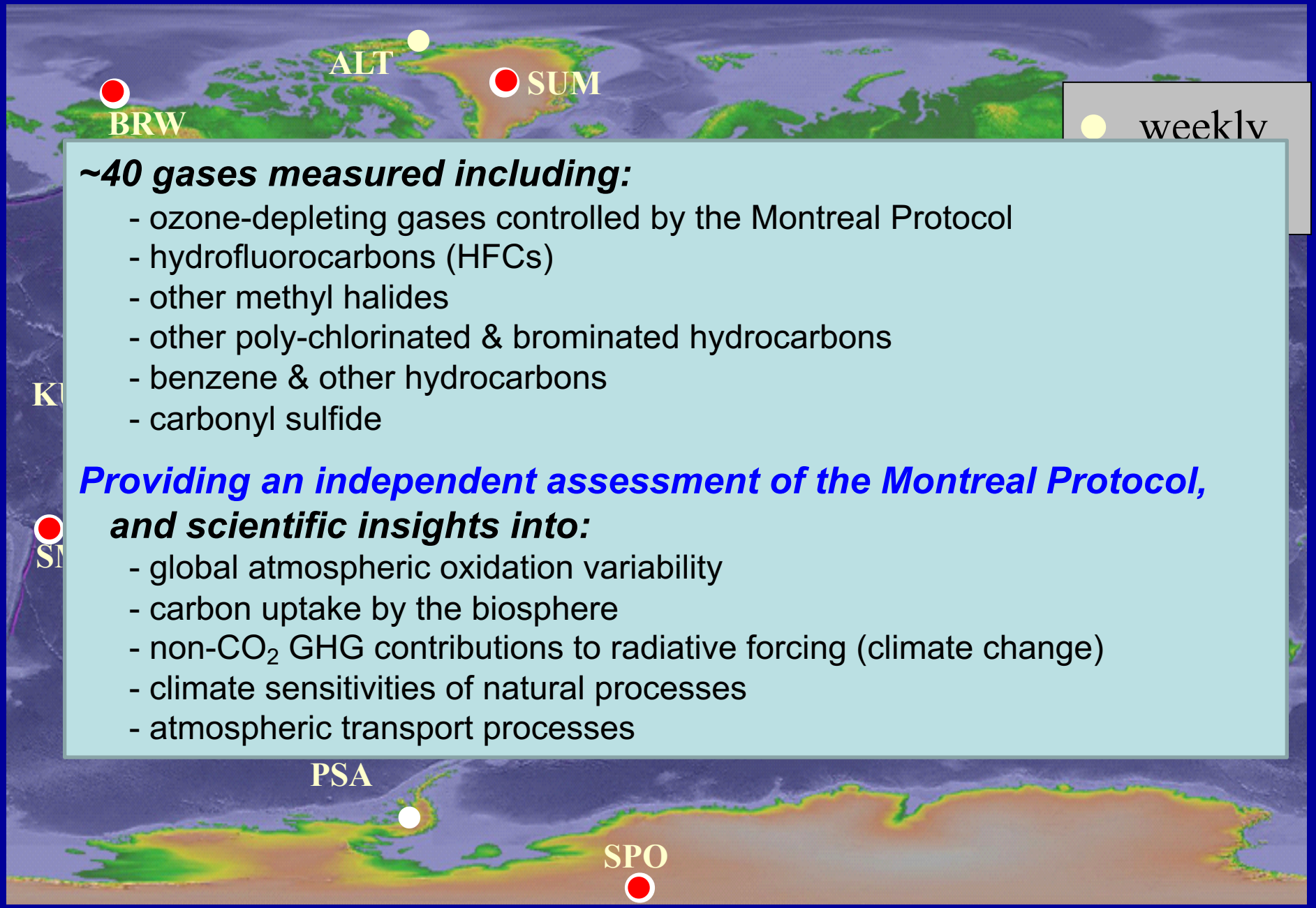
From NOAA/GMD-measured tropospheric concentrations of CFCs, HCFCs, chlorinated solvents, methyl halides, halons

→ Pre-ozone-hole concentrations of ODSs are projected for later in this century (WMO reports),

provided continued adherence to the Protocol's controls

(see updates at http://www.esrl.noaa.gov/gmd/odgi/)

NOAA/GMD: Tracking ozone-depleting gas concentrations globally



~40 gases measured including:

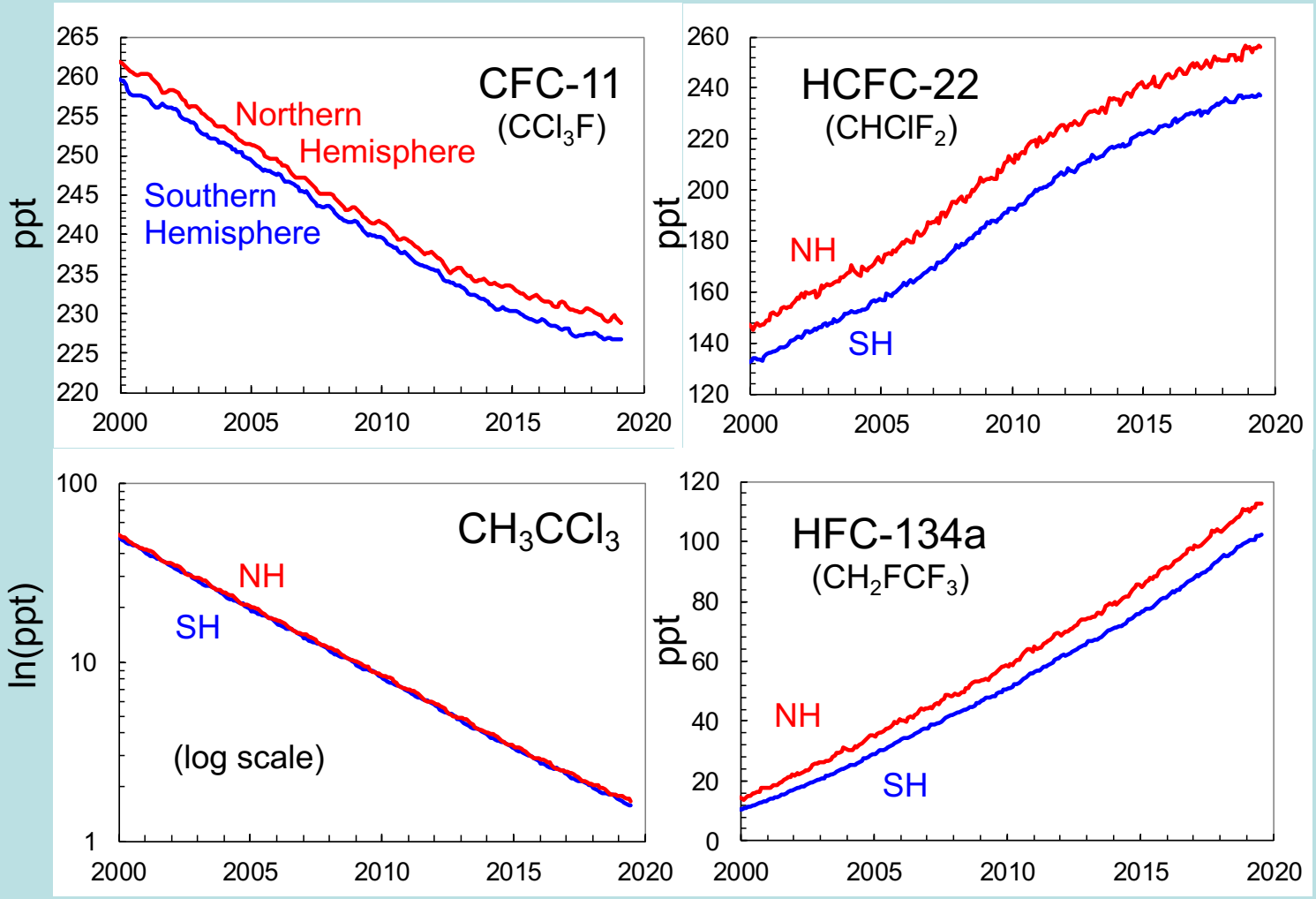
- ozone-depleting gases controlled by the Montreal Protocol
- hydrofluorocarbons (HFCs)
- other methyl halides
- other poly-chlorinated & brominated hydrocarbons
- benzene & other hydrocarbons
- carbonyl sulfide

Providing an independent assessment of the Montreal Protocol, and scientific insights into:

- global atmospheric oxidation variability
- carbon uptake by the biosphere
- non-CO_2 GHG contributions to radiative forcing (climate change)
- climate sensitivities of natural processes
- atmospheric transport processes

Atmospheric measurements for tracking the effectiveness of the Montreal Protocol

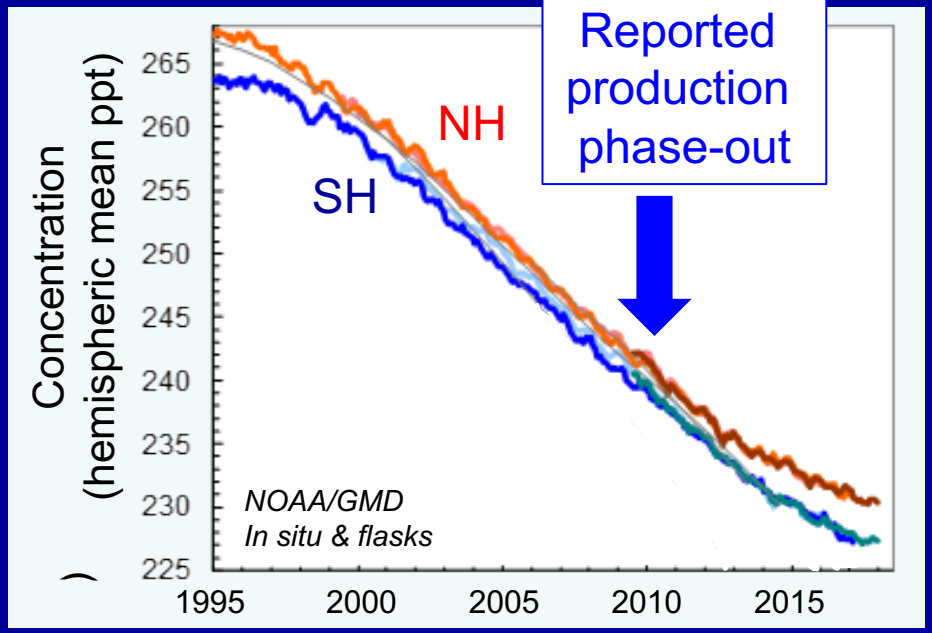
CFCs, CH_3CCl_3, *etc.* → HCFCs → HFCs → HFOs



Chemical lifetimes range from 5 to 50 years

NOAA/CIRES flask data

Atmospheric CFC-11



CFC-11:

→ ***Second most abundant ODS; accounts for 20-25% of*** ozone-depleting chlorine

→ ***Was the largest contributor to the overall decline*** of atmospheric Cl from 2007-2012

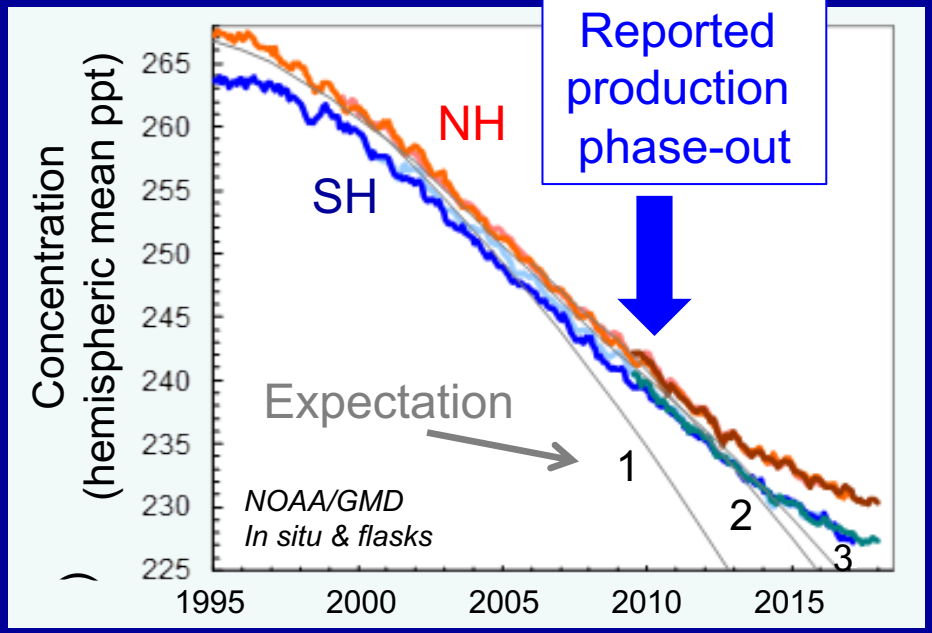
→ ***While production was reportedly phased out in 2010, significant emissions persist,*** primarily from a foam "bank" of ~900 kt currently

After a production phase-out:

* concentration decline ***should have accelerated*** as bank becomes depleted by emissions…

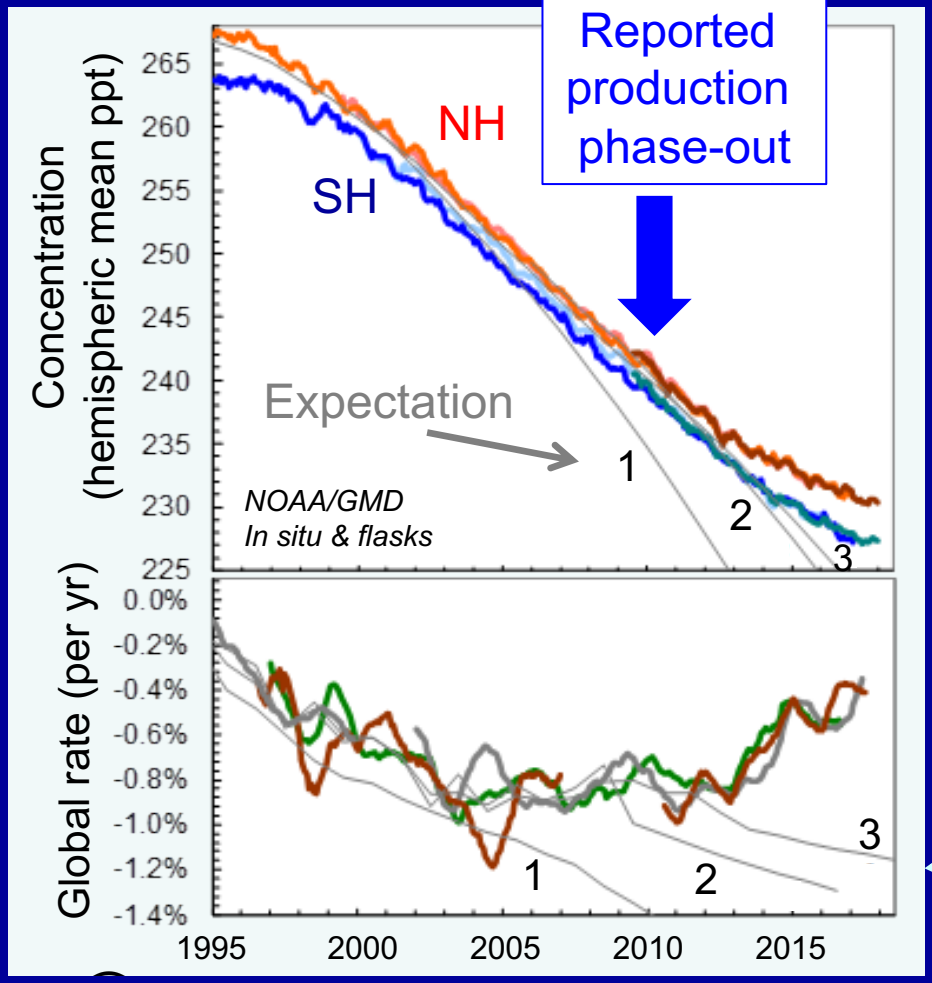
(the zero-emission limit is –2%/yr given its 50 yr lifetime)

Atmospheric CFC-11



Hemispheric mean concentration

Atmospheric CFC-11

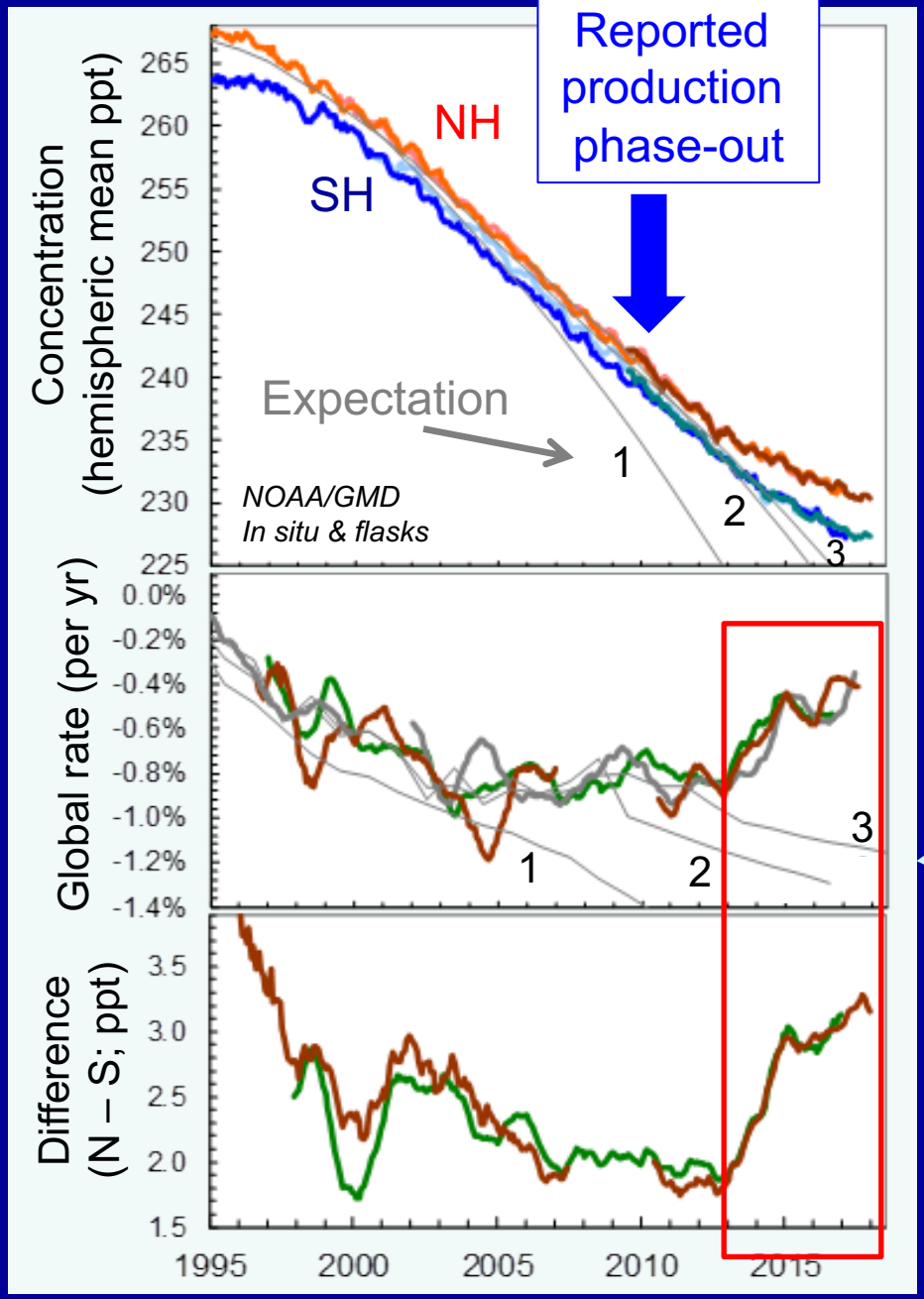


Hemispheric mean concentration

Global rate of change

Expectation

Atmospheric CFC-11



Hemispheric mean concentration

Global rate of change

Expectation

Hemispheric concentration difference

→Qualitatively consistent with an increase in NH emissions

Why the unexpected slowdown?

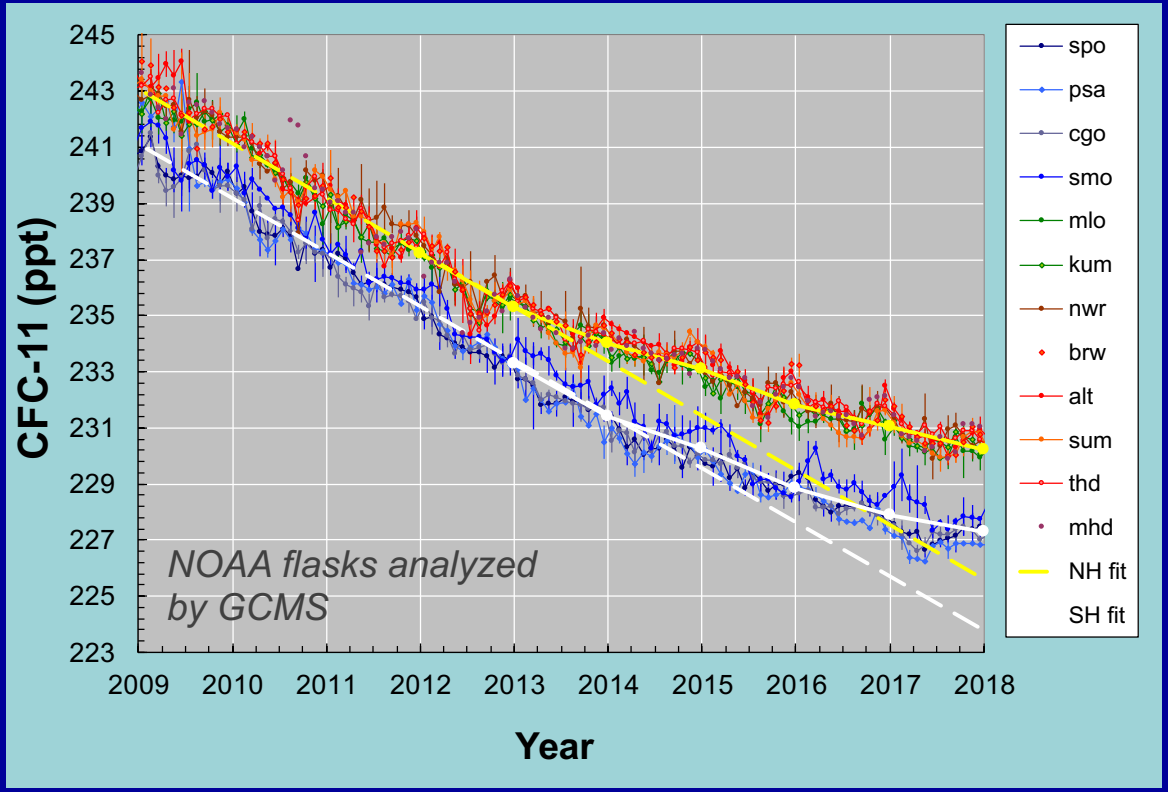
Consider the evidence:

It does NOT seem to be a measurement problem:

→ slowdown observed by independent measurements (NOAA and AGAGE) using multiple techniques, and in different aspects of the data

It is NOT unique to certain sites, it is observed everywhere

→ initially in the NH, and then later in the SH



Why the unexpected slowdown?

What does it imply about global emission rates?

Considering a mass balance approach to CFC-11 in the global atmosphere:

$$dG_{F11}/dt = Emission - G_{F11}*k_{F11}$$

$$dG_{F11}/dt = Emission - G_{F11}/\tau_{F11}$$

Where
G_{F11} = global CFC-11 mass
k_{F11} = pseudo 1st-order loss rate constant
τ_{F11} = global CFC-11 lifetime

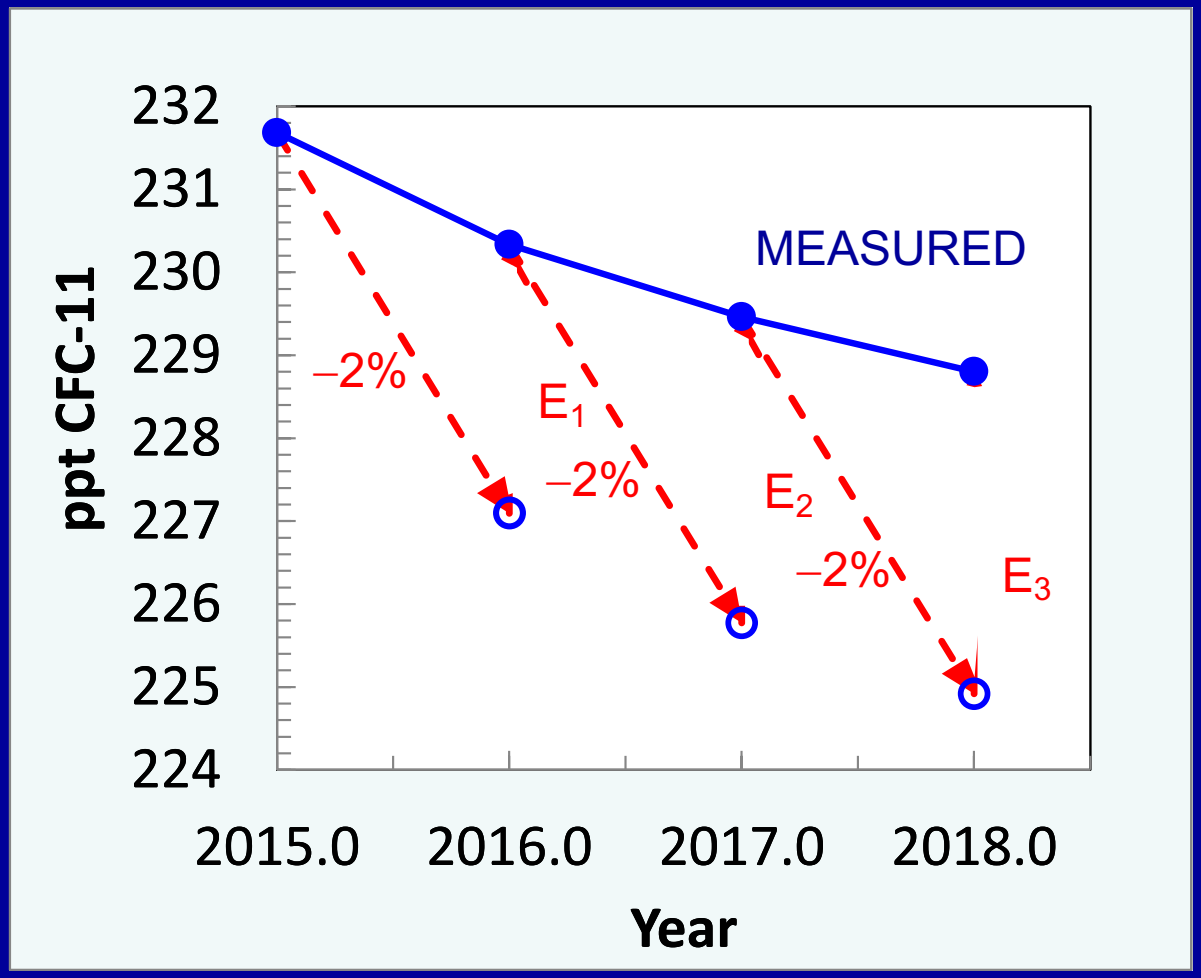
Estimated from measurements
and, typically, simple box models that:
a) constrain G and dG/dt based on surface measurements
b) constrain k and τ based on laboratory studies

Deriving emissions from concentrations

Global CFC-11 concentration changes reflect the balance of

a) **EMISSION**

b) **REMOVAL** (*lifetime* & transport)

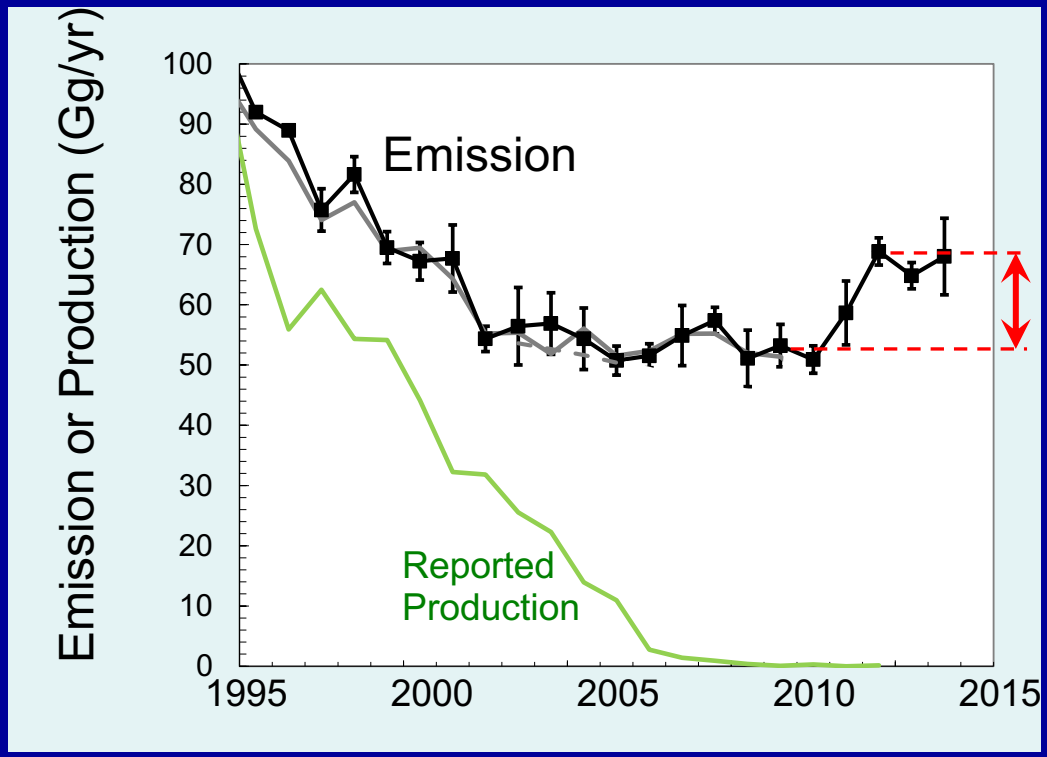


For a ~ 50 yr lifetime, atmospheric concentrations should decline at ~1/50 yr^{-1} or 2% yr^{-1} *in the absence of emissions.*

2) The derived CFC-11 emissions history

Mass balance considerations (a simple box-model analysis):

$$dG_{F11}/dt = \text{Emission} - G/\tau_{F11}$$



Measured

13 ± 5 Gg/yr
(25%) increase

(2014-2016 *vs.* 2002-2012;
2017 is similarly elevated)

Are CFC-11 emissions *really* increasing despite the Montreal Protocol and reported phase-out by 2010?

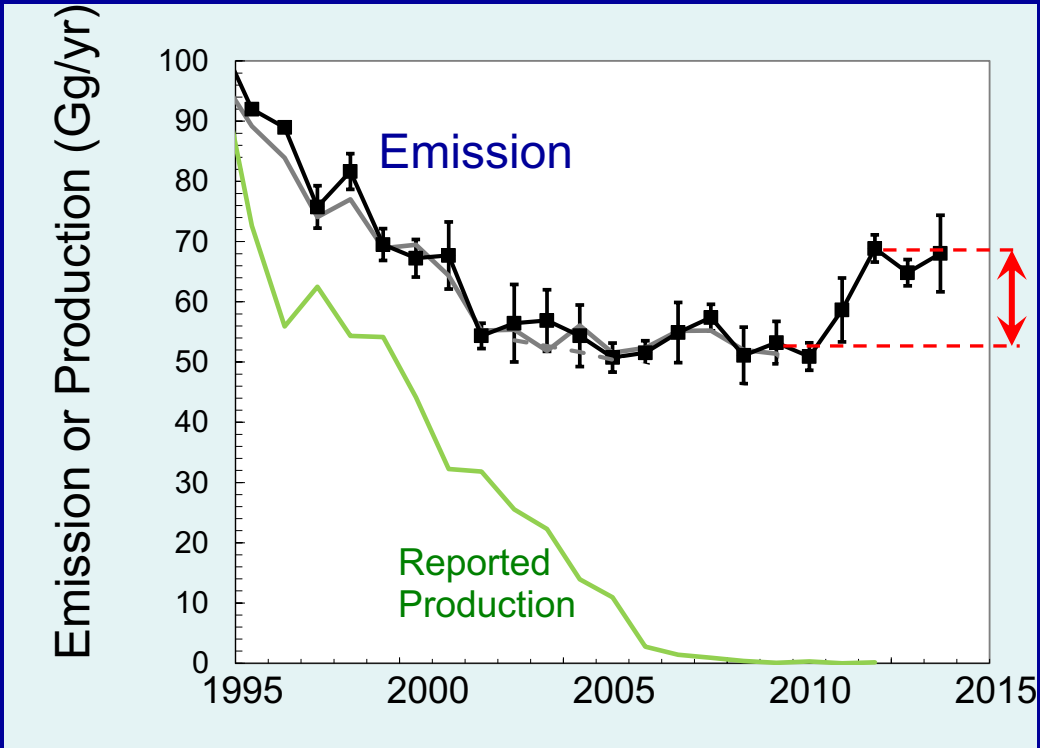
Montzka et al., 2018

2) The derived CFC-11 emissions history

Mass balance considerations (a simple box-model analysis):

dG_{F11}/dt = Emission – G/τ_{F11}

Measured



13 ± 5 Gg/yr
(25%) increase

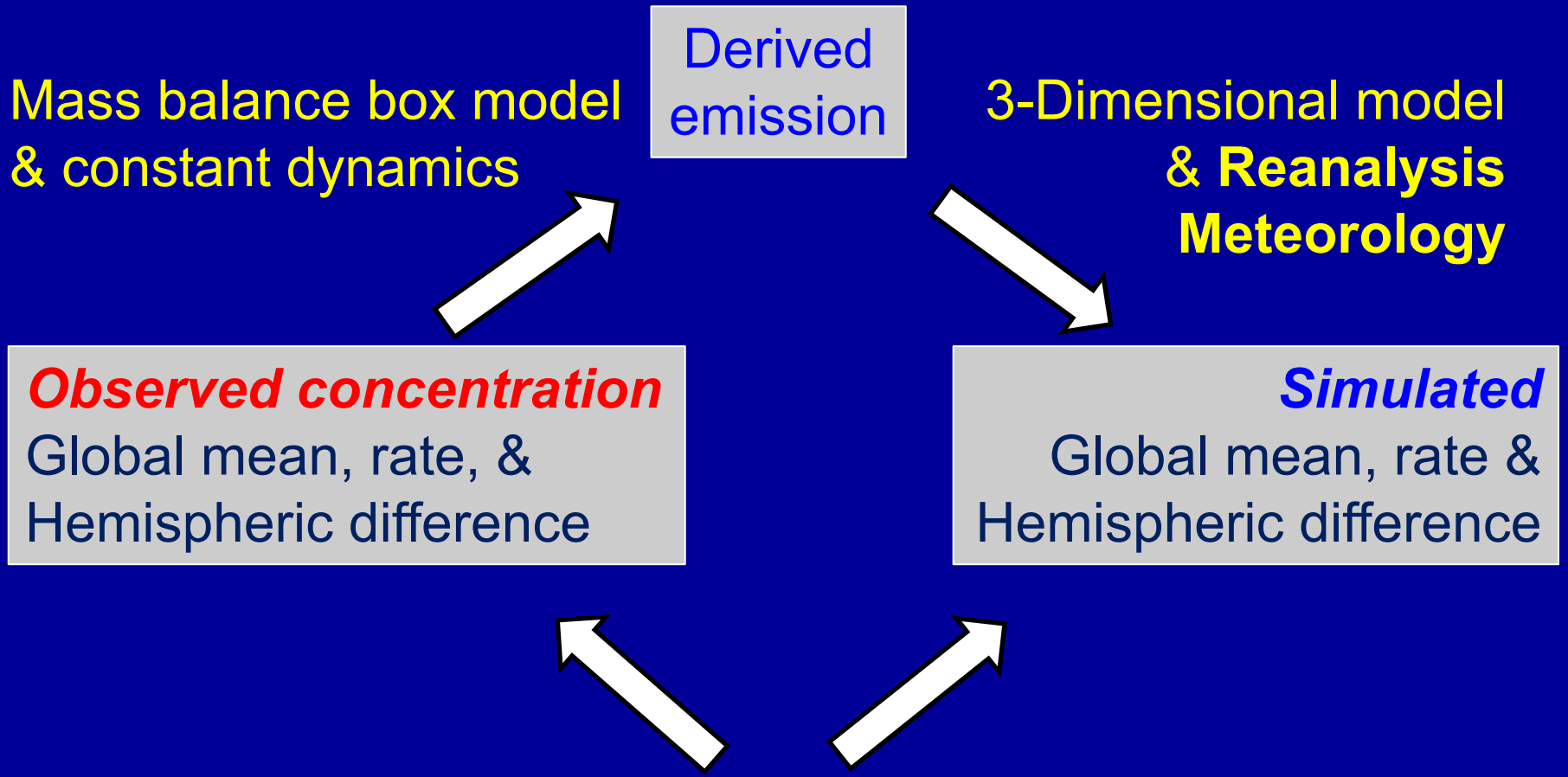
(2014-2016 *vs.* 2002-2012;
2017 is similarly elevated)

Or has CFC-11 loss and transport changed ("τ_{F11}")?
→**How constant is the Brewer-Dobson circulation, or the CFC-11 lifetime?**

Montzka et al., 2018

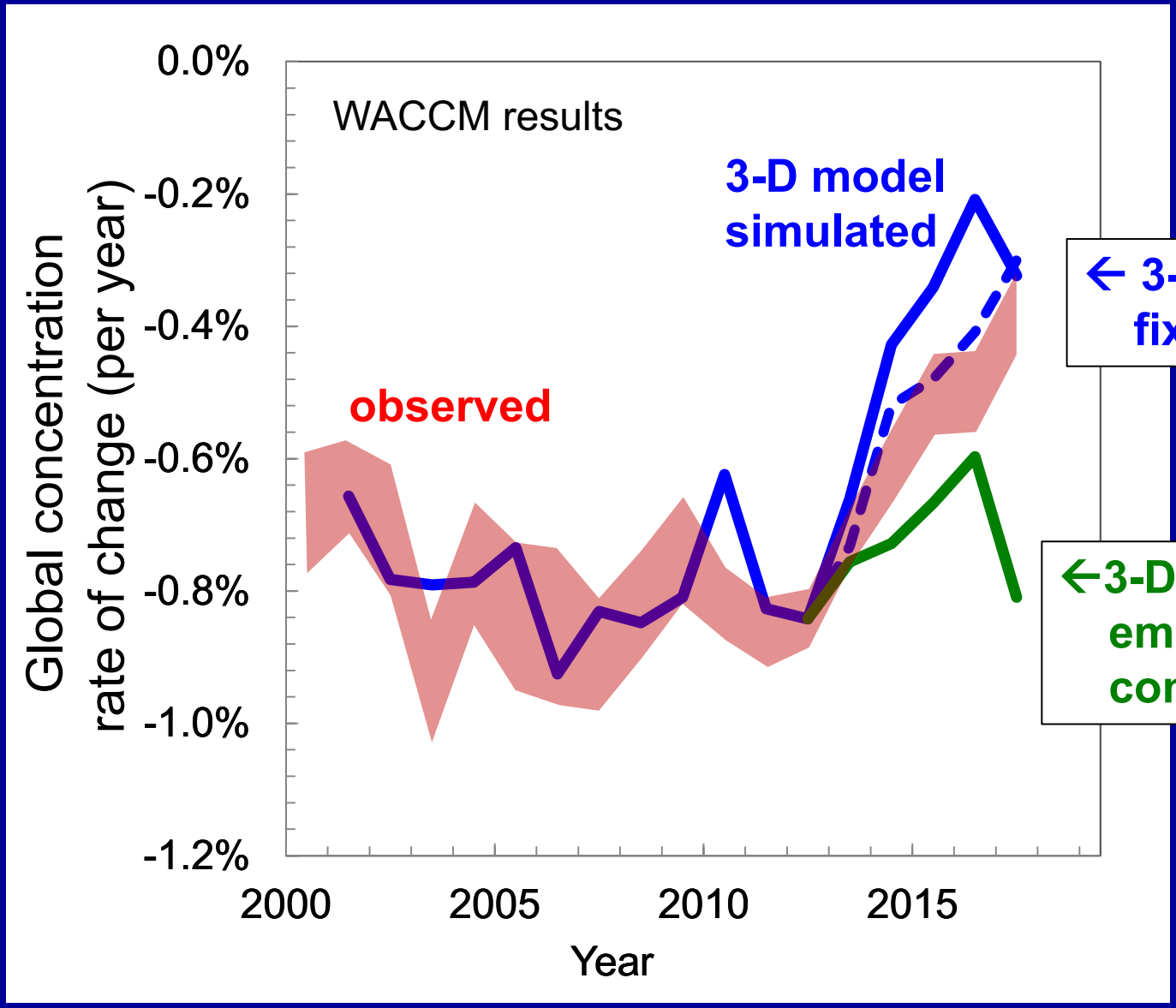
Taking a closer look with 3-D CCM simulations

Have changes in dynamics affected the CFC-11 decline?



→ any differences could imply dynamical influences

3-D modeling of CFC-11 global concentration decline



Montzka et al., 2018

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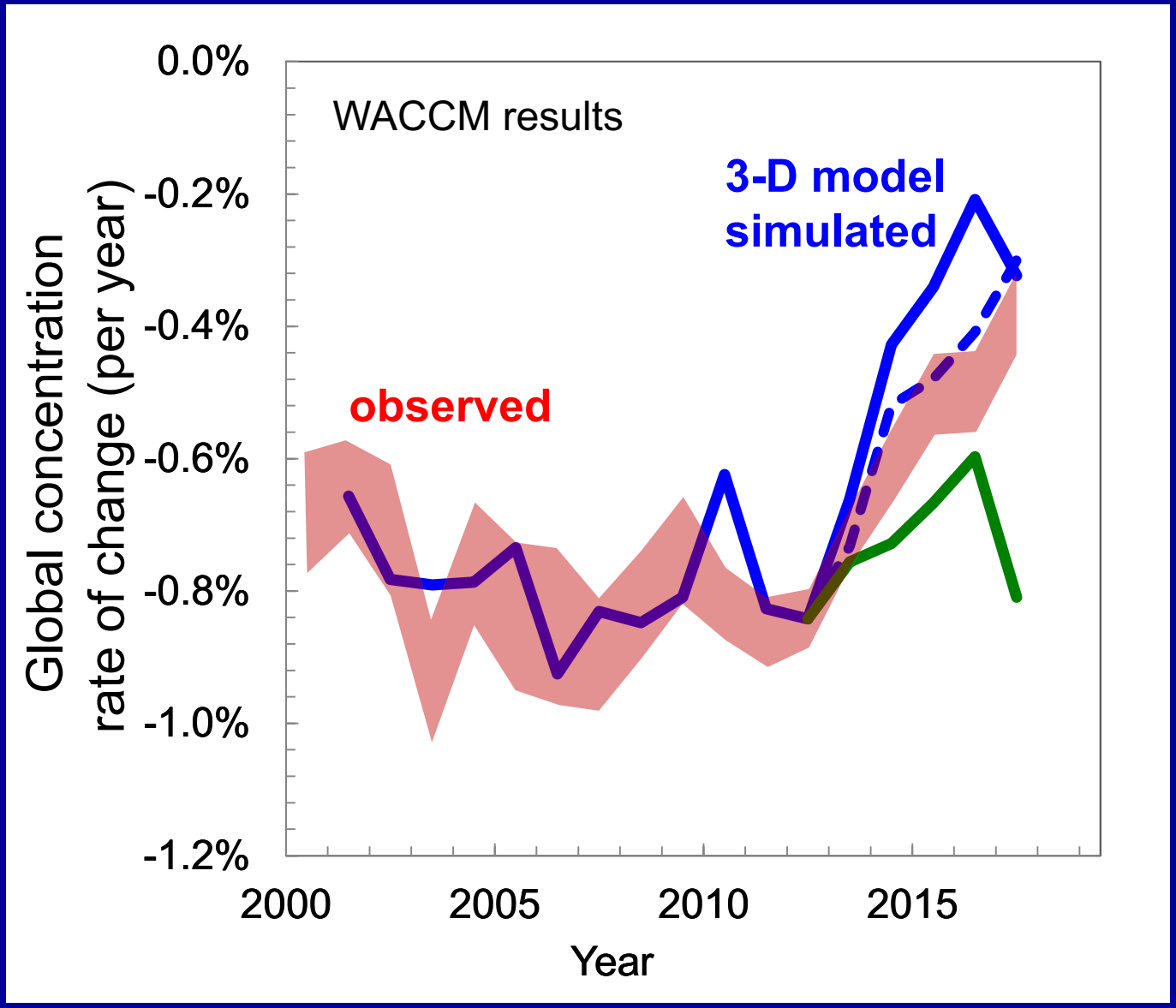


WACCM suggested a **significant dynamical contribution to the CFC-11 slowdown of ~50%** (other models suggested a smaller effect),

but **an emission increase is needed** to fit observed increases in rate and hemispheric difference

Montzka et al., 2018

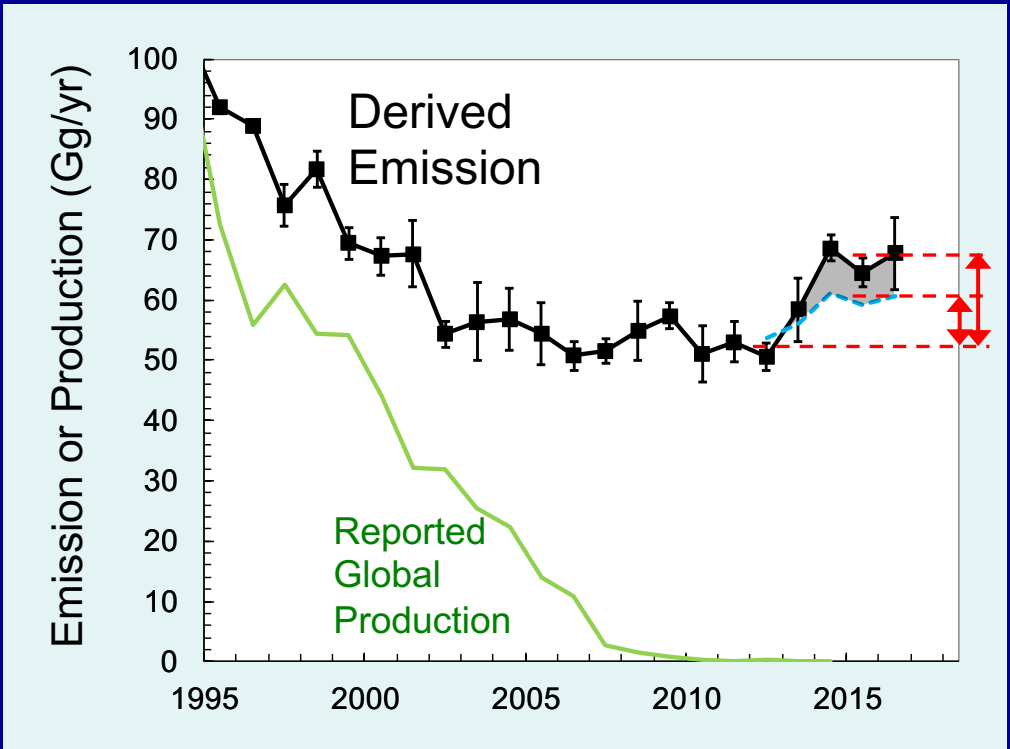
Derived CFC-11 emission

Global CFC-11 concentration changes reflect the balance of

a) **EMISSION**

b) **REMOVAL** (*lifetime & transport*)

d[CFC-11]/dt = Emission – Removal



Montzka et al., 2018

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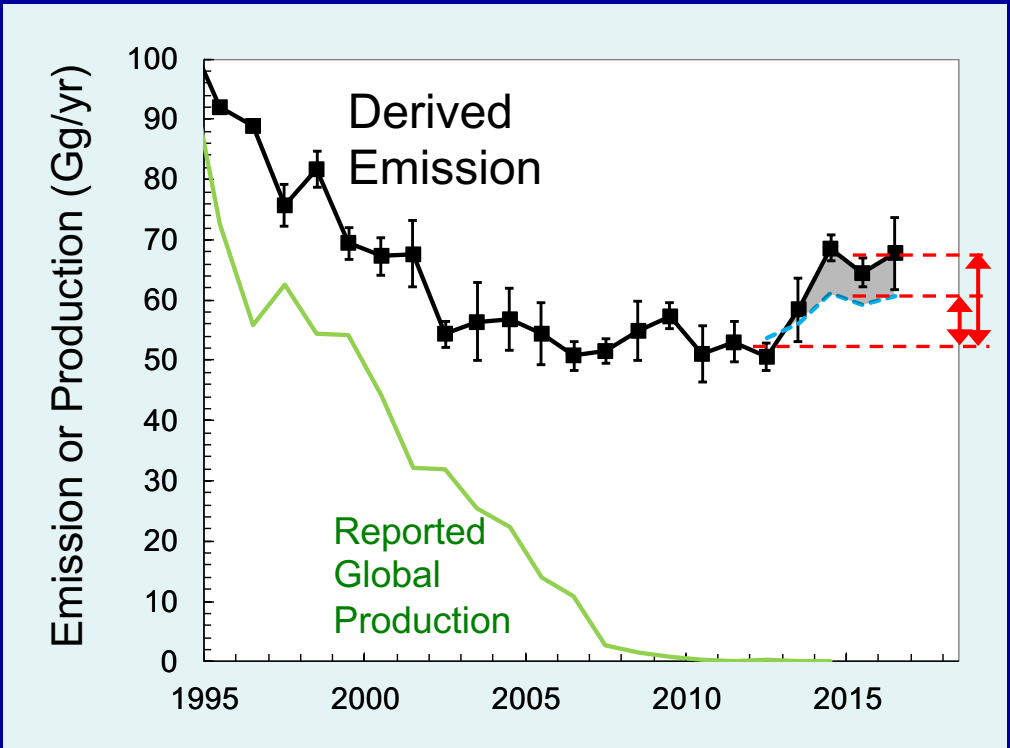

We concluded:
Emissions had increased, but up to 50% of the increases could have been from dynamics or lifetime changes…

Montzka et al., 2018

Derived CFC-11 emission

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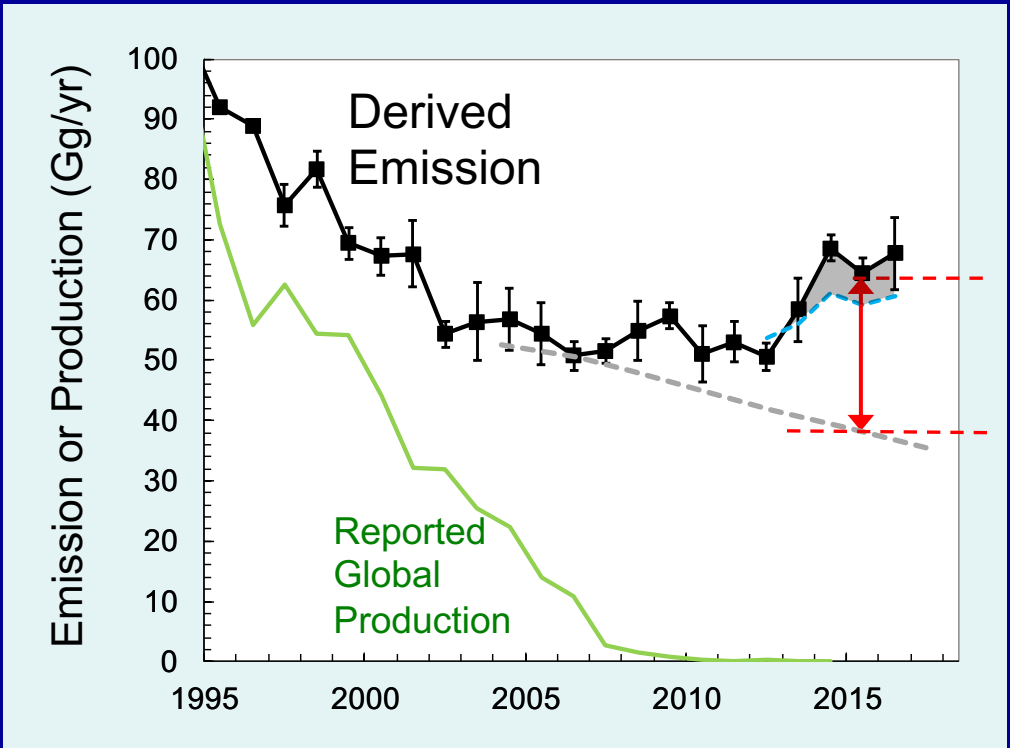

25-30 Gg/yr
above expectations…

Montzka et al., 2018

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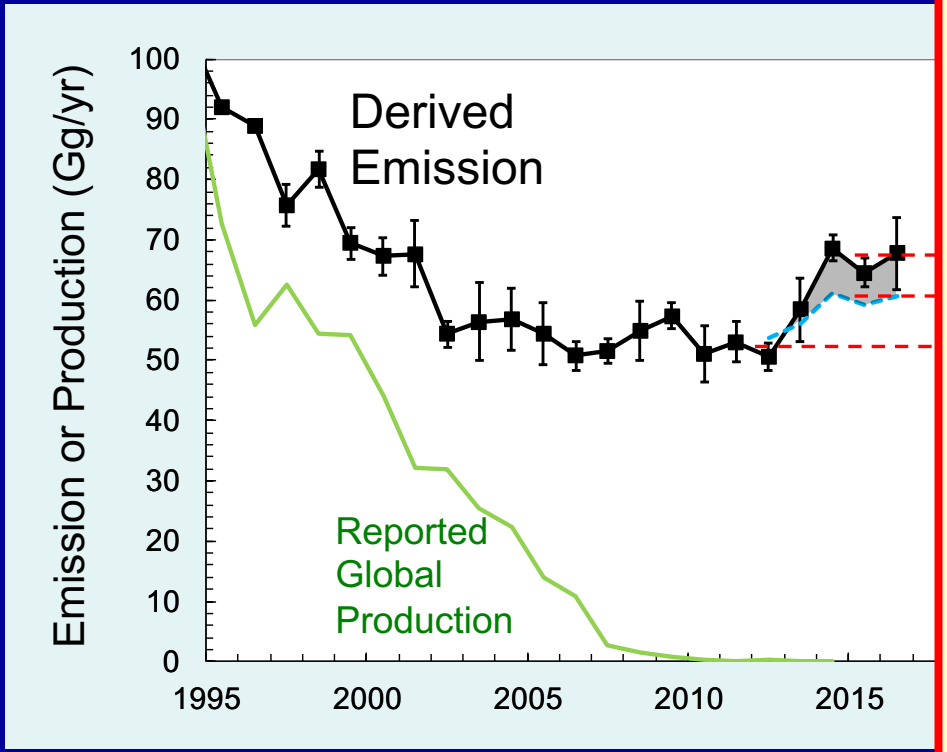


Revised Conclusion

(unpublished):

The original WACCM runs had some issues that overestimated the dynamical contribution.

Subsequent multiple model analyses reveal that any dynamical contribution to the derived emission increase is <10%.

Quantification of the emission increase becomes more accurate when averaged over more years…

Do the observations themselves suggest emissions increasing?

Air reaching Hawaii in autumn can be influenced by Eurasian emissions (Lin *et al*., 2014, DOI: 10.1038/NGEO2066).

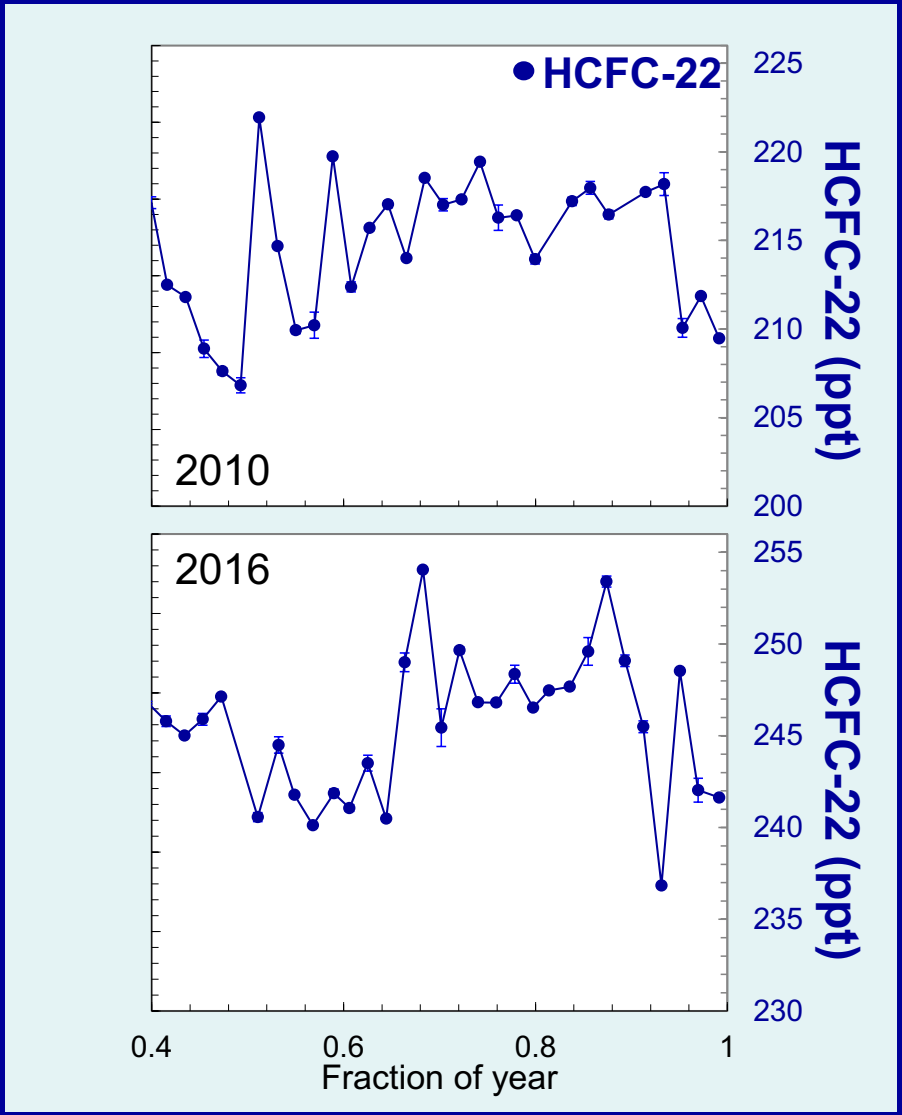
A close look at our results from the Mauna Loa station showed:

Before 2012: pollution plumes reaching Hawaii **DID NOT** contain elevated concentrations of CFC-11

After 2012: pollution plumes reaching Hawaii **NOW CONTAIN** elevated concentrations of CFC-11.

Do the observations themselves suggest emissions increasing?

Pollution plume events reaching Hawaii were identified by:



1) Increased concentrations of a number of gases:
HCFC-22, CH_2Cl_2, and CO

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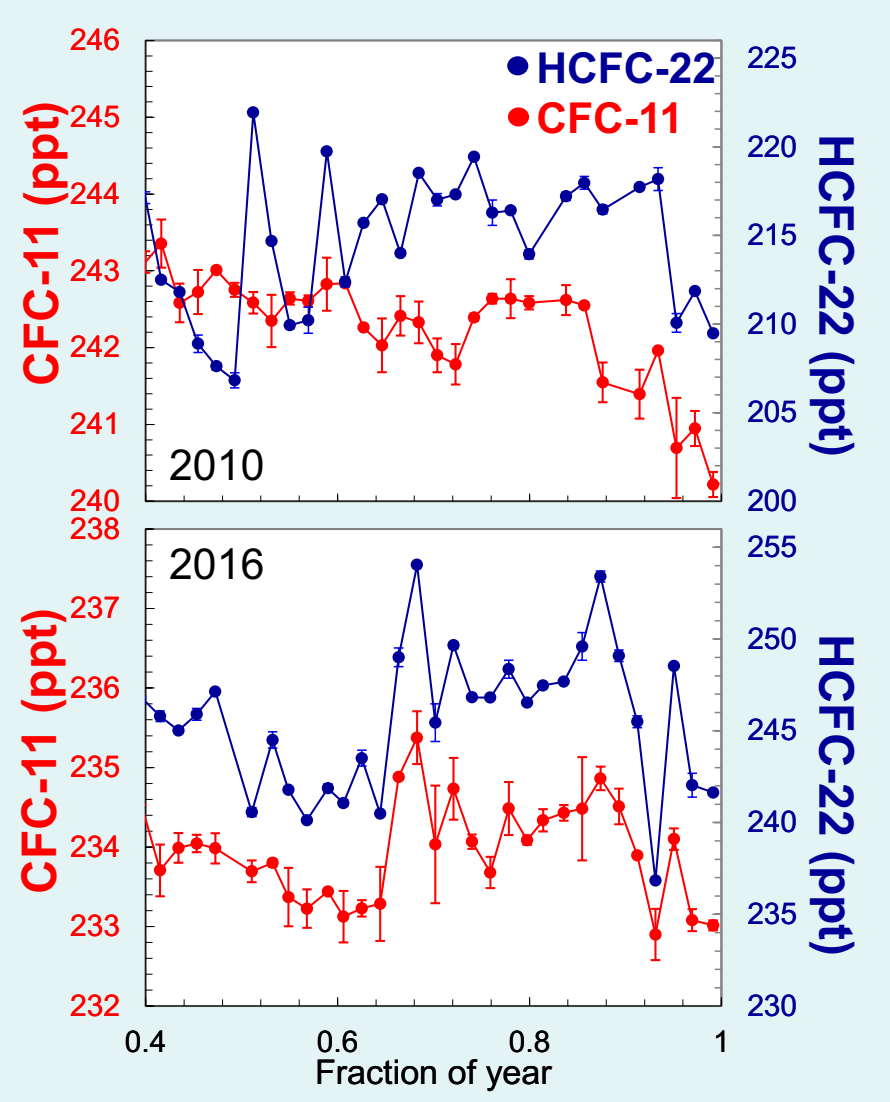
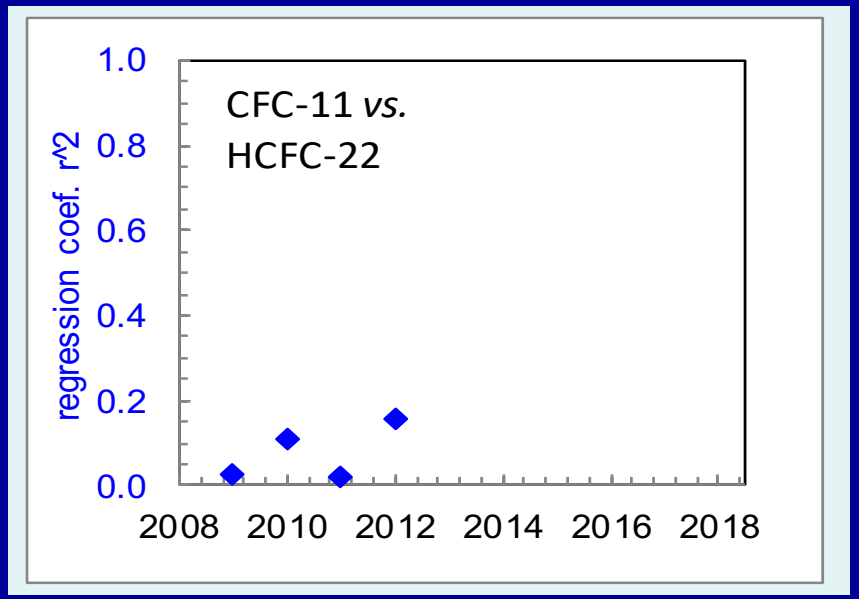


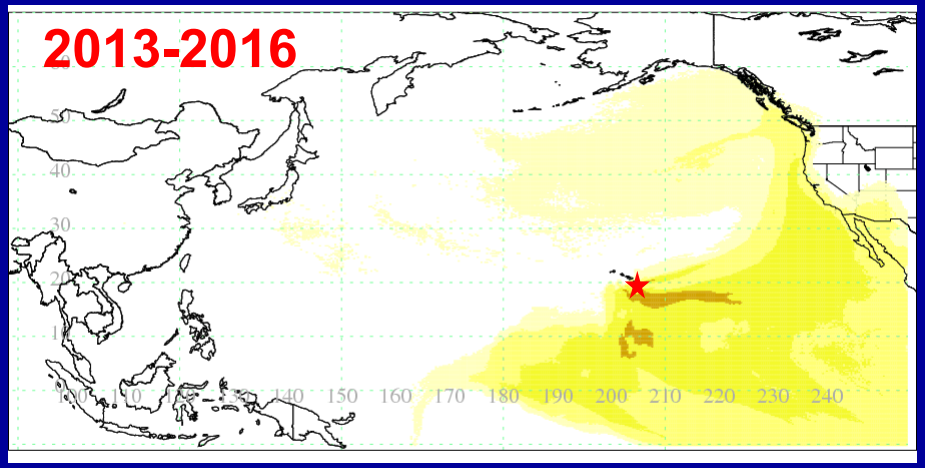


Only after 2012 do pollution plumes contain elevated CFC-11 concentrations

Correlations among HCFC-22, CH_2Cl_2, & CO are strong in all years

The source region for those pollution plumes reaching Hawaii were identified by meteorological models of air transport:

Lower [HCFC-22] & [CFC-11]



Darker colors indicate the surface region influencing samples collected in Hawaii

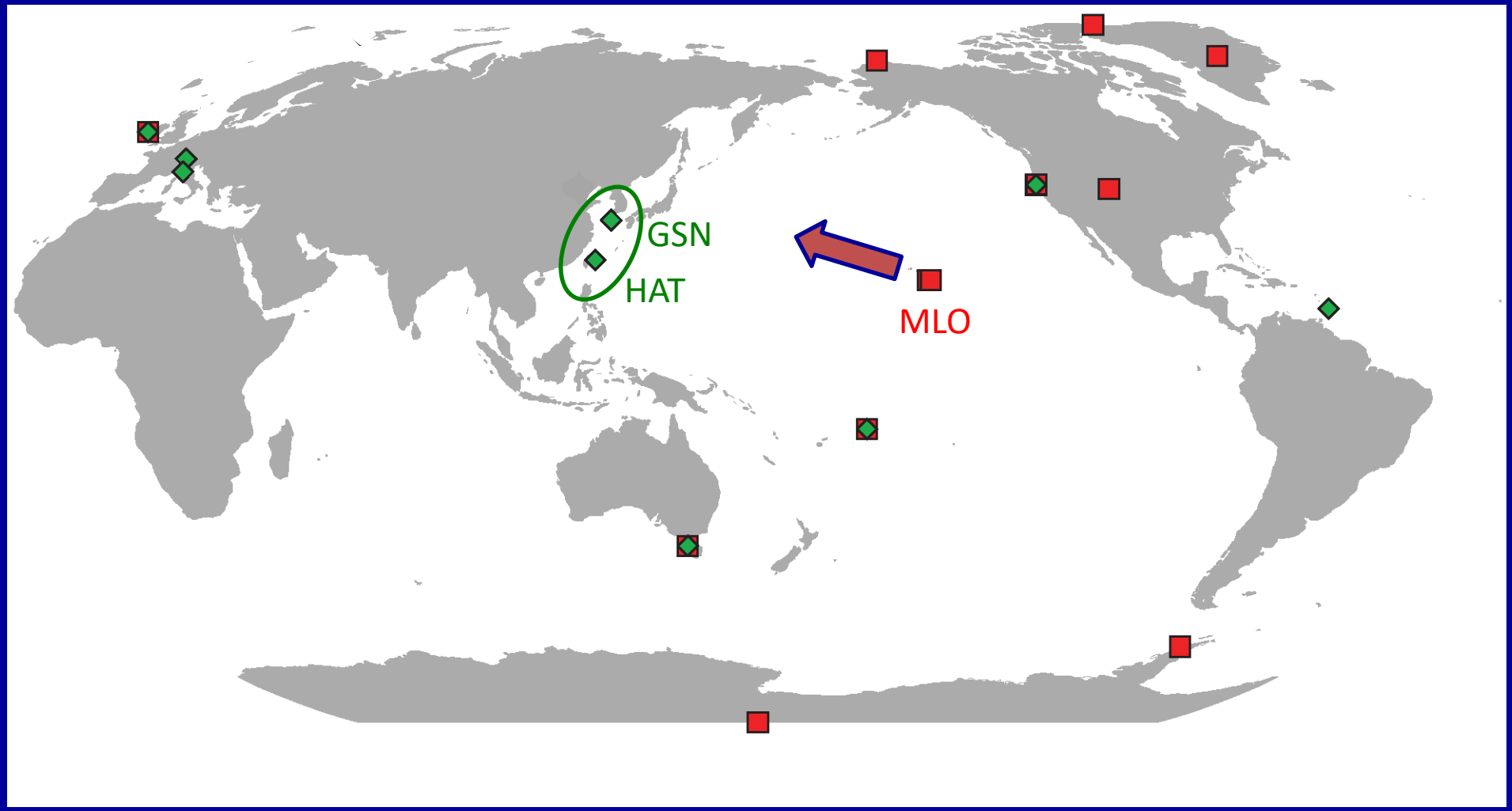
After 2012, air associated with eastern Asia contains relatively higher concentrations of CFC-11

→ Some portion of the global emission increase is from Eastern Asia

Montzka et al., 2018

In a second study (Rigby *et al*., 2019), measurements within eastern Asia are analyzed...

AGAGE & affiliates plus NOAA sampling locations (Rigby et al., 2019)

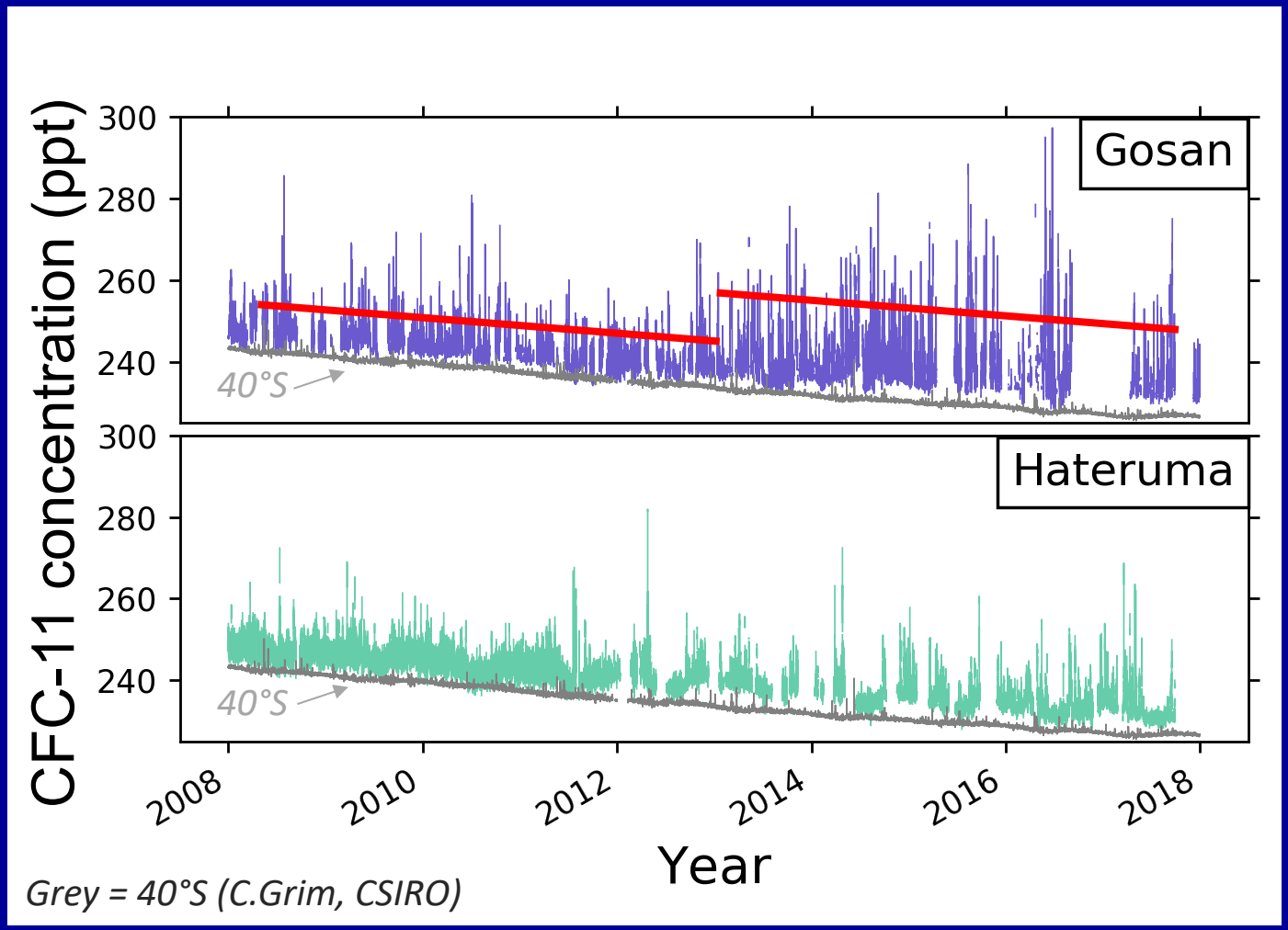


Between 12 and 34 measurements per day at AGAGE & affiliate sites

Rigby et al., 2019

From Rigby et al., 2019:

Discrete air sample results:



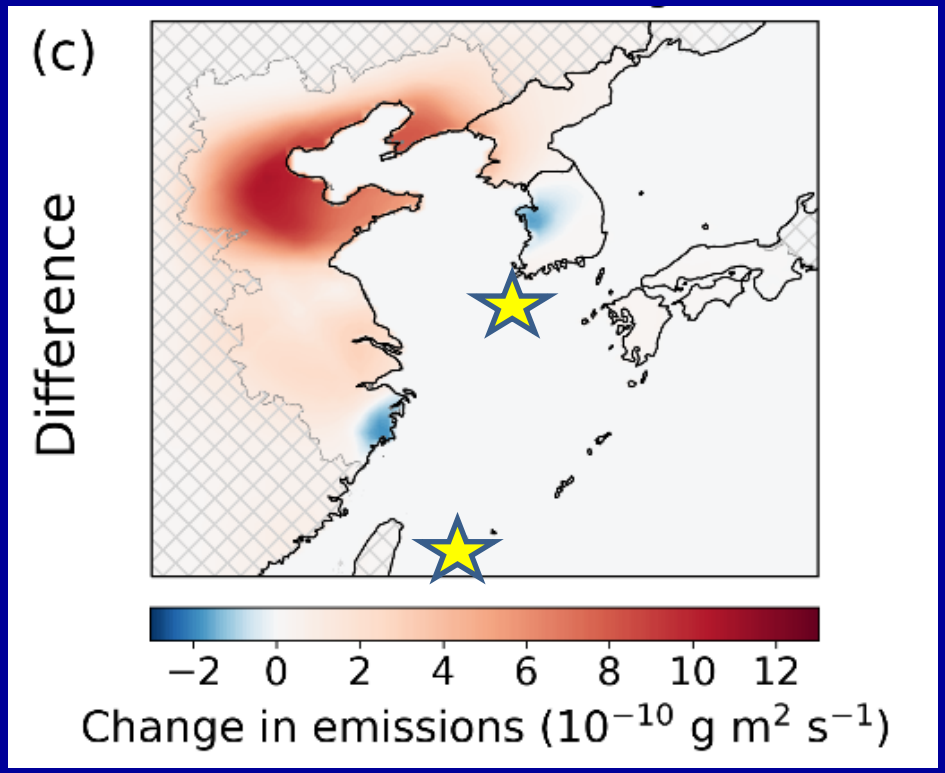
After 2012, CFC-11 concentrations are increasingly elevated in pollution plumes reaching these sites, particularly at GSN

AGAGE, R.O.K. (K.N.U.), and Japan (NIES)

Rigby et al., 2019

Inverse Lagrangian model analyses of these measurements in Rigby et al., 2019:

Red = regions where emissions increased after 2012>>



About 50% of the global emission increase comes from eastern Asia, specifically the Chinese provinces of Shandong and Hebei.
Where's the other half???

Similar inverse analyses of observations from the U.S., Europe, and Australia suggest low emissions (< 10 Gg/yr) and no recent increases.

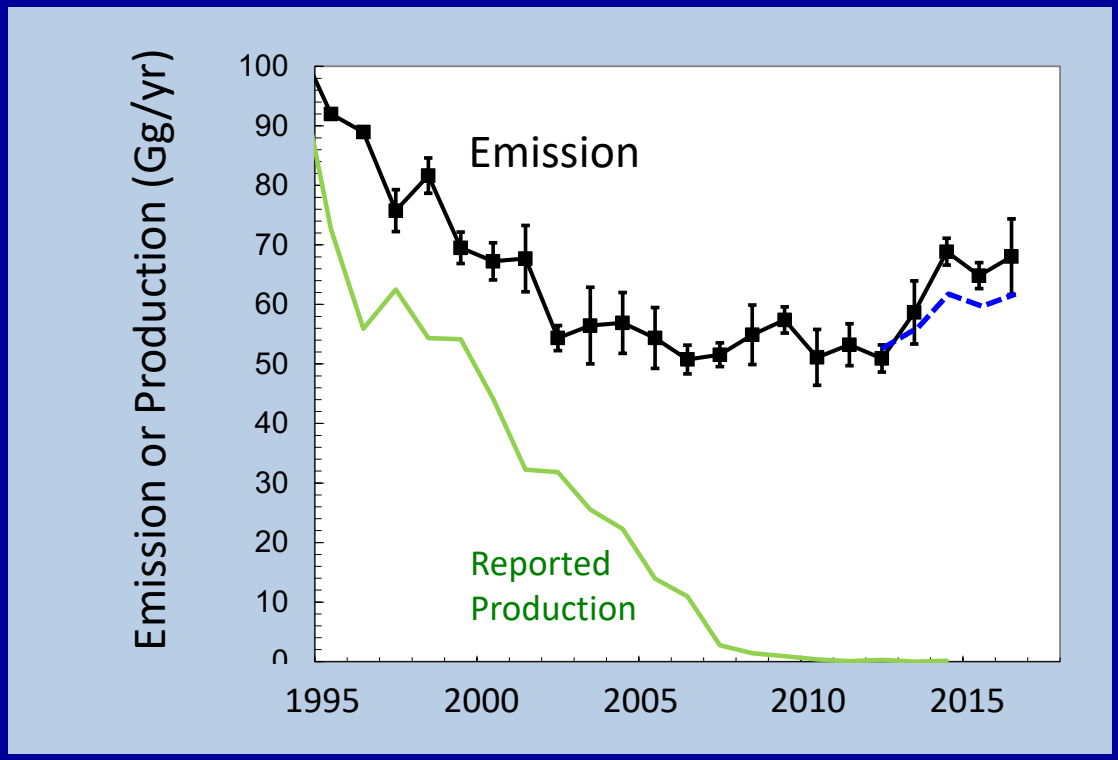
Regional estimates from many parts of the world are not possible.

Rigby et al., 2019

AGAGE data
Rigby *et al.*, 2019,
https://doi.org/10.1038/s41586-019-1193-4

2) Do the results imply renewed production?

→ is the Montreal Protocol being violated?



OR: is CFC-11 escaping more rapidly from the foam "bank" (~1200 Gg in 2012)?

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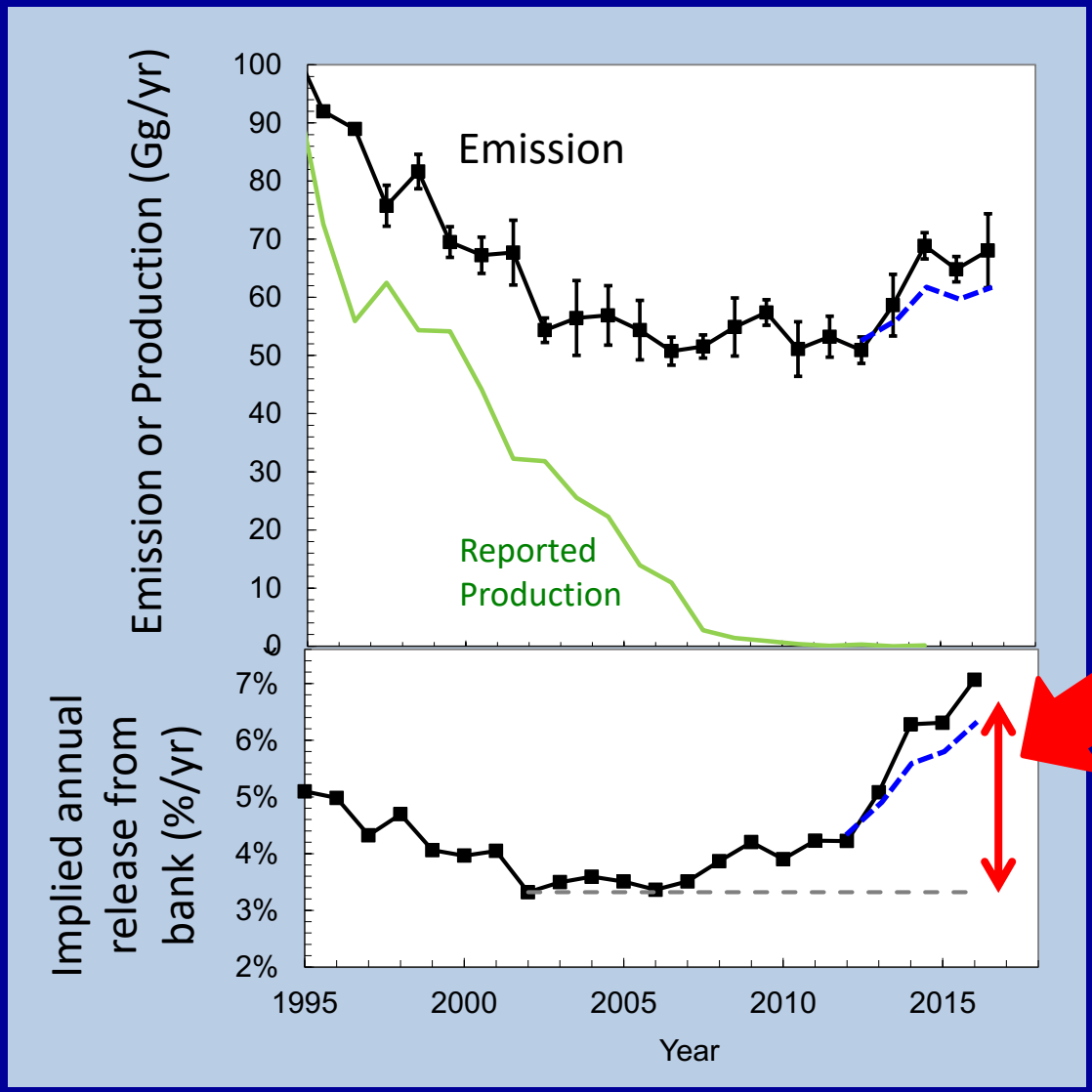


OR: is CFC-11 escaping more rapidly from the foam "bank" (~1200 Gg in 2012)?

With no new production, the escape rate from the 'bank' **would have had to nearly double since the early 2000s…**

→ this seems highly unlikely

Montzka et al., 2018

Implications for the ozone layer:

If the problem is rapidly fixed, the impact on the ozone layer should be small.

If these emissions continue → ozone recovery delay of 7 to 20 yr.

(WMO-SAP, 2018; Dhomse et al., 2019 & others)

Unlikely?

Perhaps, but the magnitude of the problem ultimately depends on the magnitude of unreported production.

Have we detected only the "tip of the iceberg"??

Most likely use of the new production:

Polyurethane insulating foams *(WMO-TEAP; 2019)*

→ if so, then, emissions detected are << associated production.

and enhanced emissions could be sustained even with effective mitigation.

25-30 Gg/yr ***emissions*** for foams implies

→ **50-100** Gg/yr of CFC-11 ***production*** (peak prod. was 400 Gg/yr)

Global reaction to our results:

On-the-ground investigative reporting by the NY Times and EIA

→ evidence for ongoing use and production of CFC-11 in China

→ *Overall quantities unknown…*

Ozone-Harming Gas Is Detected, Despite Ban

By Henry Fountain, NY Times
p. A4, May 16, 2018

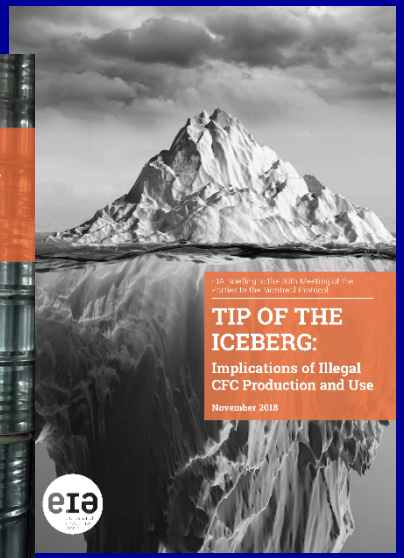
An Environmental Win Falters. Why? Some Clues Point to China

By Chris Buckley and Henry Fountain, NY Times
p. A1, June 24 2018

More Evidence Points to China as Source of Ozone-Depleting Gas

By Chris Buckley and Henry Fountain, NY Times
p. A14, November 3, 2018

…and the EIA



The EIA suggests that in 2018 ***most*** of the closed-cell foam industry in China had reverted back to using CFC-11

But this was from a very limited survey of users…

The Parties to the Montreal Protocol consider the findings in their annual meetings in 2018 and 2019:

Ecuadorian President Mr. Lenín Moreno and meeting co-chairs open the meeting

Science Assessment Panel members (+ Dave F.)

Presenting the science to the Parties in side events

Remaining questions:

What is being done about the issue?

The Parties to the Montreal Protocol are:

* ***taking the issue seriously*** (recent meetings dominated by this issue)
* ***looking for more information*** (meetings held, reports requested)
  - what will be the ozone layer impact? Are emissions increasing outside of NE China? What led to the issue? How is the CFC-11 being produced?

…to facilitate rapid mitigation of the issue

They are also:

* ***reconsidering $$ being transferred to China*** via the Multi-lateral Fund (the Protocol's fund for assisting developing countries with compliance; $1.3 billion was dispersed to China via the MLF since the 1980s…)
  - China's most recent funding allotments were substantially reduced

* ***considering punitive action*** (remedial too?)

* ***considering amendments to the Protocol*** to prevent future violations
  - for ODSs, and wrt the HCFCs phase-out and HFC phase-down

(similar if not larger challenges to monitor adherence to these control schedules seem likely…)

China's response:

Has repeatedly indicated a commitment to work with other countries, scientists, and industry experts to locate and eliminate the true source of the increased CFC-11 emissions.

Has conducted inspections of 1,172 enterprises across the country, and found instances of illegal production and use (and prosecuted those responsible), but amounts were small (29.9 tonnes and 10 enterprises)

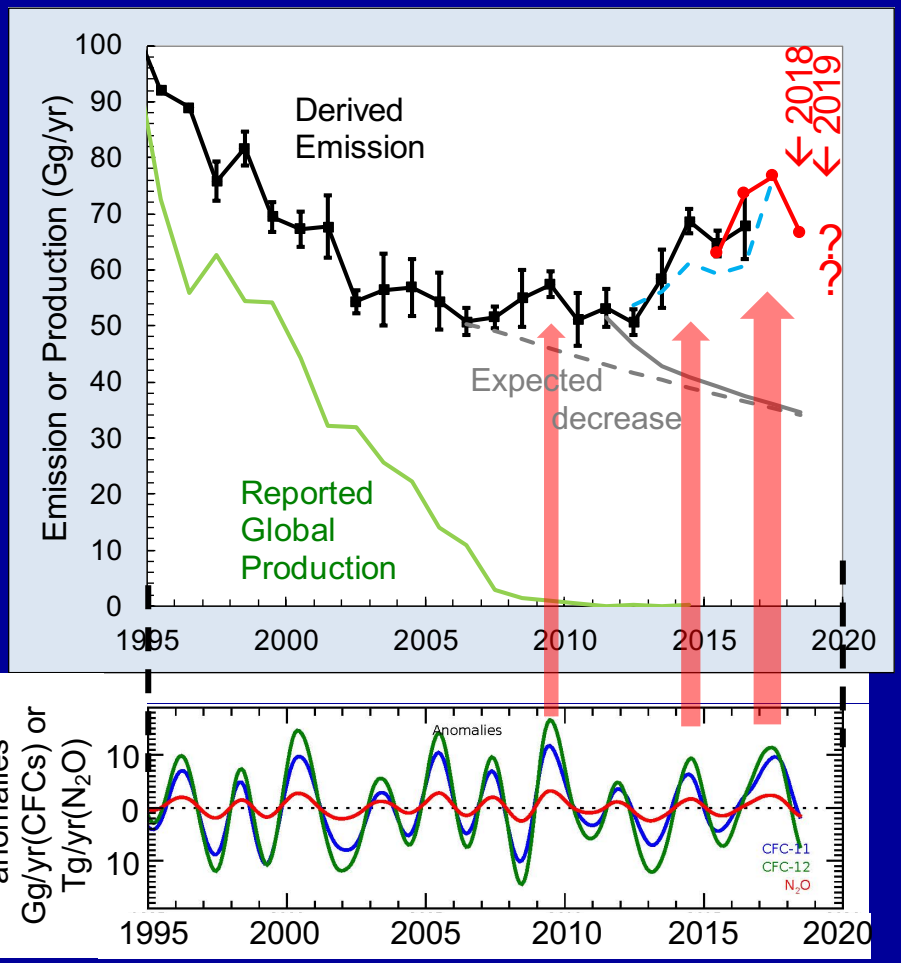
→ not enough to account for atmosphere-based results?

Has formulated a plan of action (with international input and before the Rigby et al paper fingering China in particular) that involves:

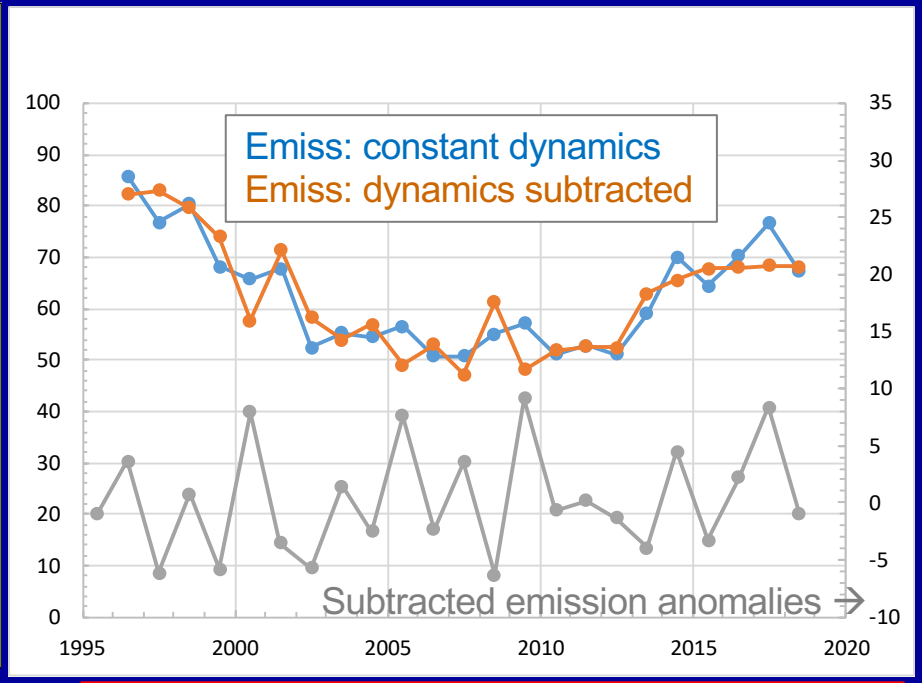
- **Developing national-scale atmospheric monitoring** of ODSs and HFCs
- **Building 6 testing laboratories** (will help with enforcement)
- **Strengthening inspections and enforcement** (ecology and environment bureaus, but difficult as businesses are many and officials are few)
- **Better tracking of CCl_4** (source material)
- **New programs to enhance enforcement**
- **Facilitating reporting of non-compliance** by industry (e.g., competitors)
- **Extending penalties to end-users** for non-compliance

How have things changed since 2017?

with constant dynamics in 3 or 12 box model:



Recalculating emissions with WACCM-derived QBO-related flux anomalies subtracted from the derived box-model results:



Emission variability in recent years is reduced &
an apparent decrease in 2018 goes away…

Ray *et al.*, 2020; QBO-related biases on derived annual emission estimates are possible

Concluding remarks:

State-of-the-art atmospheric monitoring and modeling enabled:

- → the early detection of a significant violation of the Montreal Protocol
- → an indication of the location of the renewed source of CFC-11
- → the Parties to consider potential revisions to strengthen the Protocol

That's all good, but the path to rapid and lasting mitigation remains unclear

→ are there other regions contributing to the increased CFC-11 emissions?

> the delay in ozone layer recovery is not yet well constrained…

More broadly, considering the future:

is our atmospheric "vigilance" capability up to the task (obs., models)?

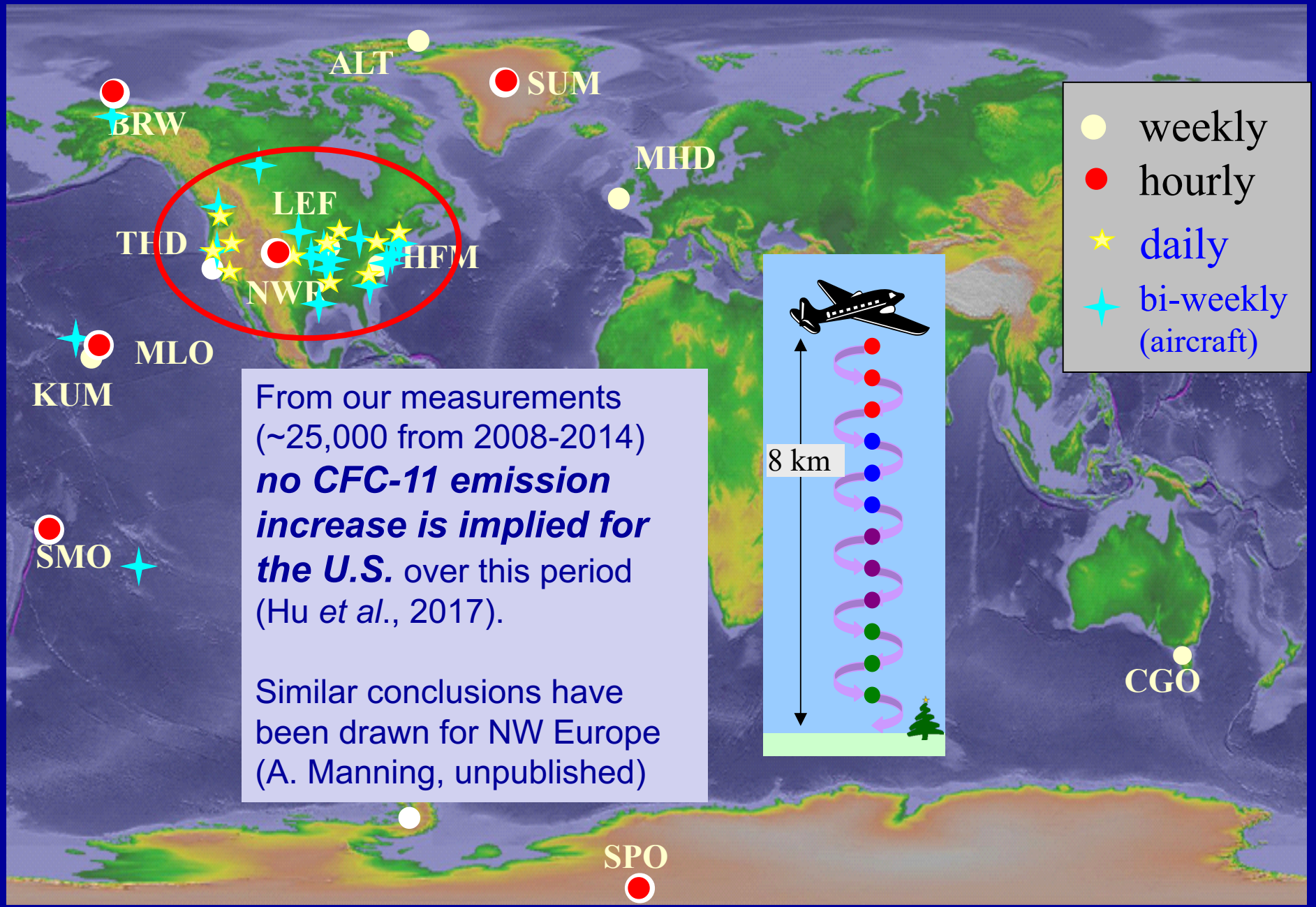
→ HCFC phase-out, HFC phase down…

→ ***greenhouse gases*** whose budgets are much more complex?

If we hope to provide actionable information to policymakers in the future our science capabilities need improving, especially in their ability to quantify, locate, and attribute emissions on global to regional scales.

Thanks for your attention

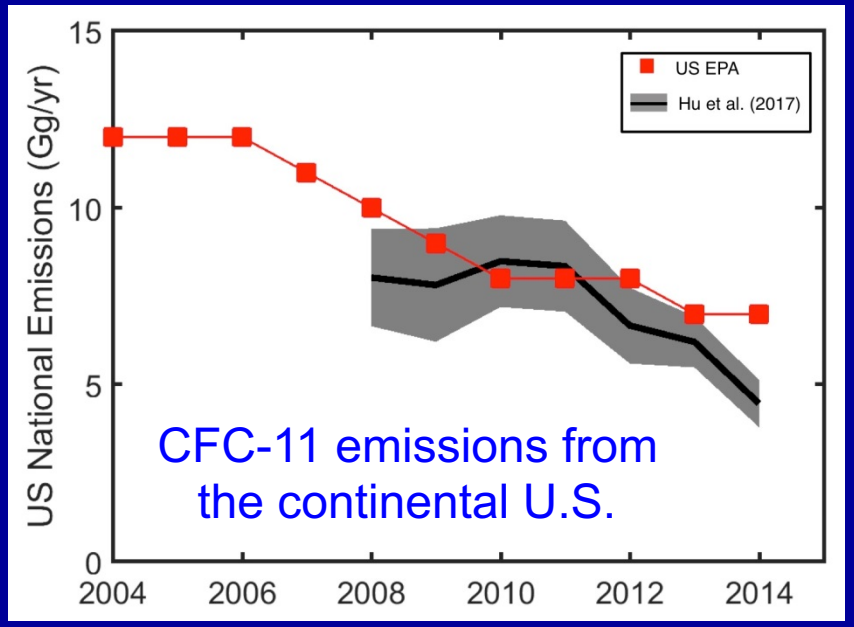
Can we locate the region where emissions are increasing?



From our measurements (~25,000 from 2008-2014) ***no CFC-11 emission increase is implied for the U.S.*** over this period (Hu *et al.*, 2017).

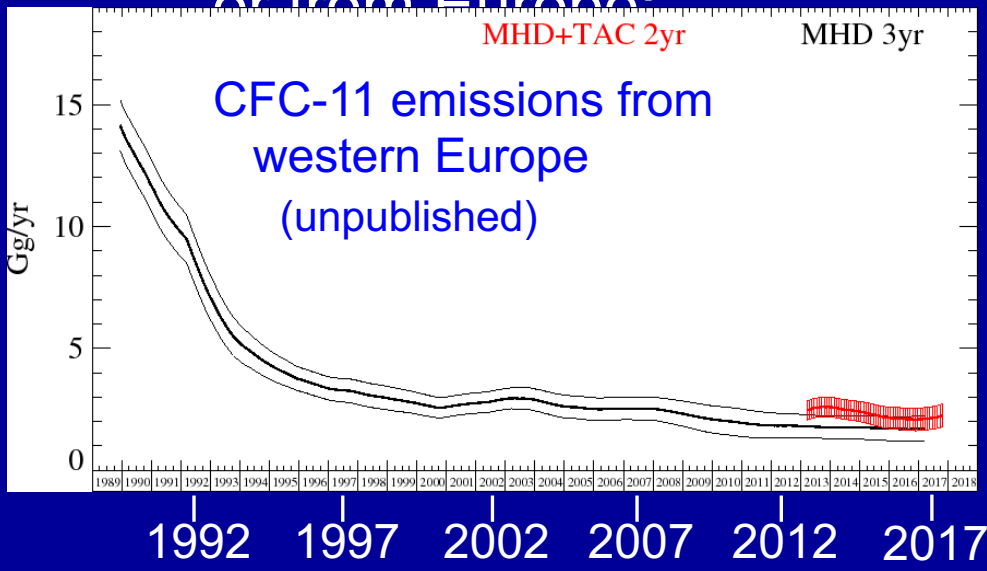
Similar conclusions have been drawn for NW Europe (A. Manning, unpublished)

* ***No significant emission increases*** are derived from the U.S. based on inverse analyses of these measurements



Hu *et al.*, *GRL*, 2017
Derived from measurements (20 sites) over the U.S. (NOAA)

or from Europe:



A. Manning (UK Met Office): Derived from measurements (sites MHD and TAC) with procedures to estimate UK emissions of all non-CO_2 Kyoto Protocol gases. These are reported annually in the UK National Inventory Report to the UNFCCC.

Quantifying magnitudes and locations of emissions with inverse modeling of atmospheric concentration data

Four components:

→ **Atmospheric concentration data:**
- → Two independent measurement locations and programs (GSN and HAT)

→ **Meteorological data:**
- → UK Met Office Unified Model (3 hr, ~0.6→0.1º longitude x 0.4→0.1º latitude)
- → ECMWF (0.2º x 0.2º over NE China, 1ºx1º over the globe)

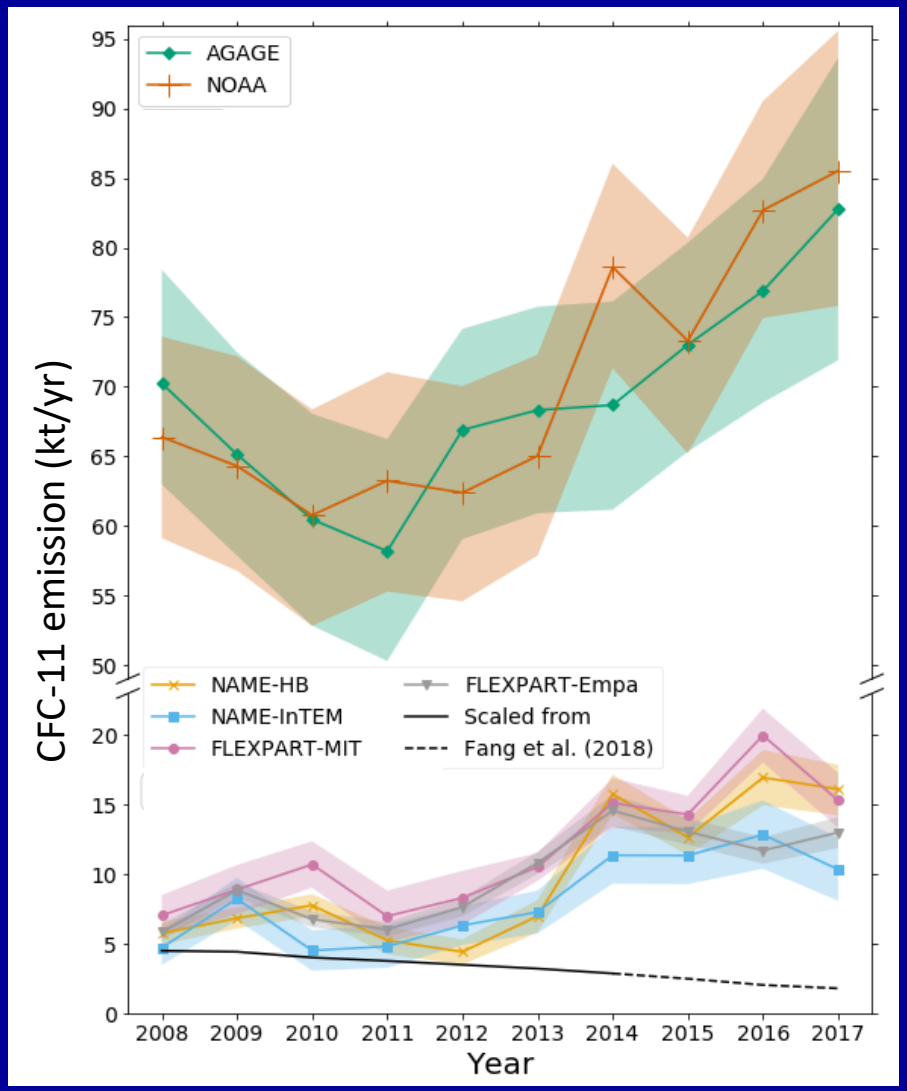
→ **Lagrangian transport models:**
- → NAME driven with UK Met Office Met. data
- → FLEXPART driven with ECMWF Met. data

→ **Inverse modeling frameworks:**
- → NAME/InTEM (Met Office); NAME-HB (U. Bristol); FLEXPART-Bayesian1 (MIT); FLEXPART-Bayesian2 (Empa)

In Rigby et al., four different state-of-the-art inversion systems were used to derive emission estimates based on measurements at GOSAN and HATERUMA

Emissions derived from FOUR different Inversion approaches

(averaged over MULTIPLE years for TWO different time intervals)



Global totals from NOAA and AGAGE (Montzka et al., SAP 2018) updated beyond 2016:

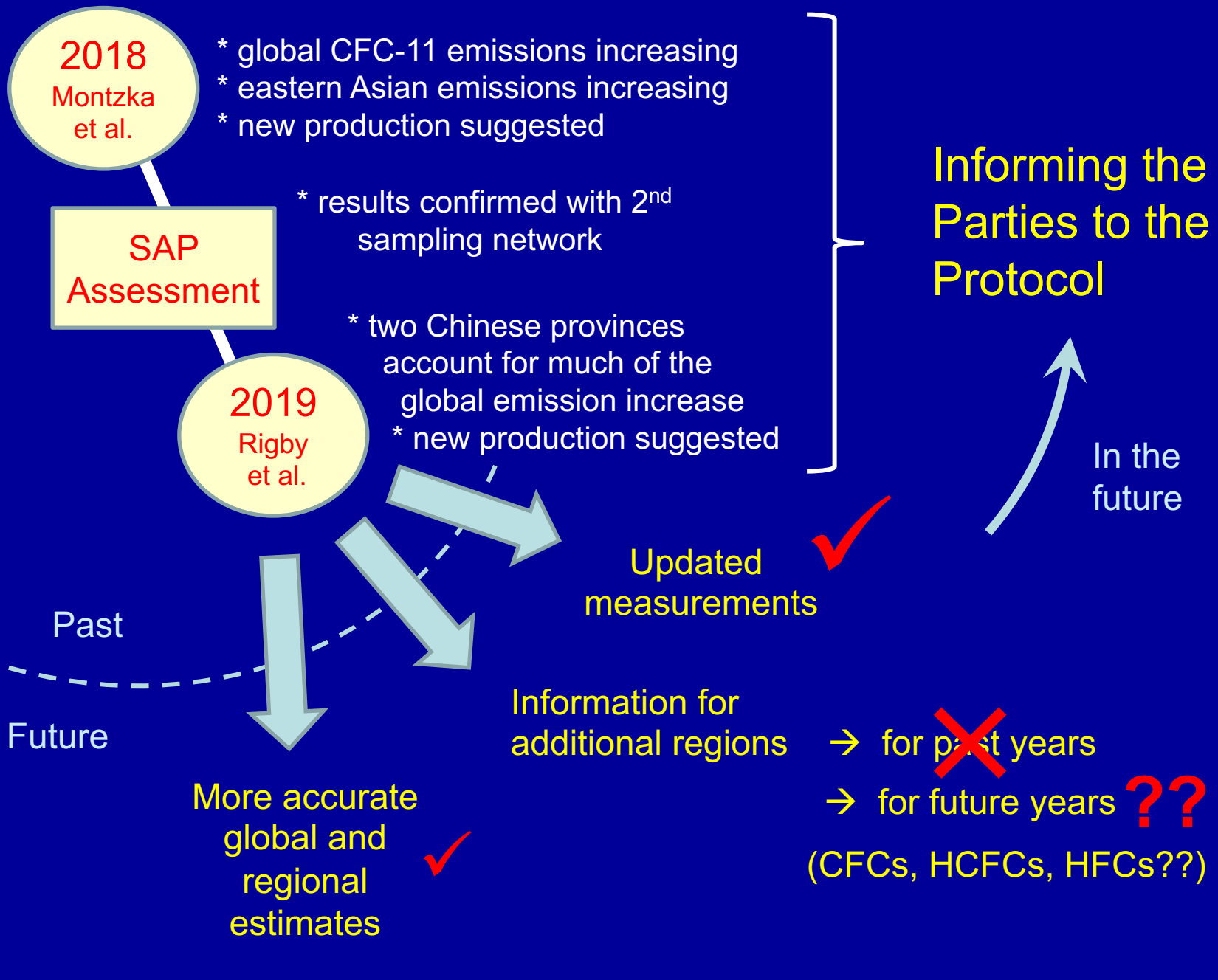
→ emissions in 2017 remain elevated.

Eastern mainland China

Solid black line is inventory-based estimate

Figure 2, Rigby et al., 2019

Prospects for improved future understanding



Recap of the scientific capabilities that allowed us to discern a substantial violation of the Montreal Protocol:

a) Sustained global-scale observations:

- Long-term, highly consistent, global coverage, redundancies within and among independent groups

b) Sustained regional-scale observations:

- long-term, in many regions of interest

c) Global Modeling expertise

d) Regional inverse modeling expertise

*(both relying on including accurate meteorological reanalysis data)**:***

- enabling quantification and spatial attribution of regional emissions

Only possible with sustained efforts over decades to enhance our understanding of measurement science and the physics and chemistry of the atmosphere on global-to-regional scales…