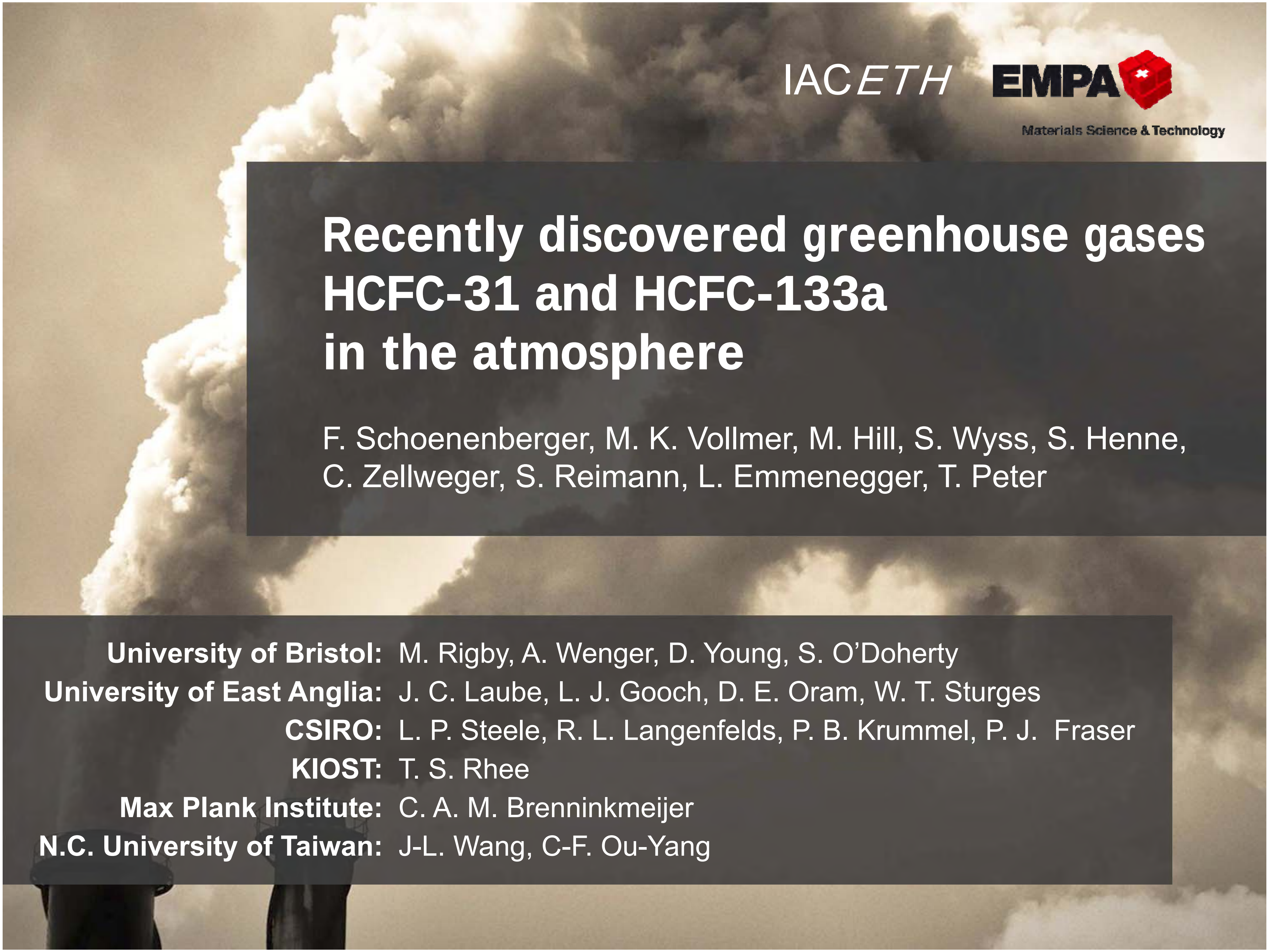

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EMPA Materials Science & Technology

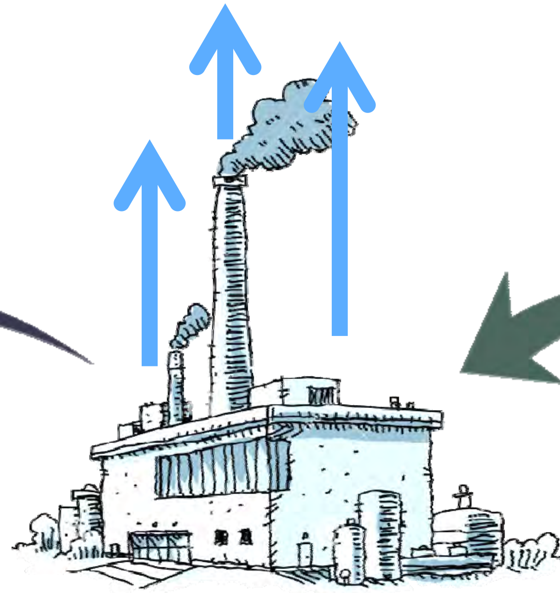
Recently discovered greenhouse gases HCFC-31 and HCFC-133a in the atmosphere

F. Schoenenberger, M. K. Vollmer, M. Hill, S. Wyss, S. Henne, C. Zellweger, S. Reimann, L. Emmenegger, T. Peter

University of Bristol: M. Rigby, A. Wenger, D. Young, S. O'Doherty
University of East Anglia: J. C. Laube, L. J. Gooch, D. E. Oram, W. T. Sturges
CSIRO: L. P. Steele, R. L. Langenfelds, P. B. Krummel, P. J. Fraser
KIOST: T. S. Rhee
Max Plank Institute: C. A. M. Brenninkmeijer
N.C. University of Taiwan: J-L. Wang, C-F. Ou-Yang

Motivation

Identify, monitor & serve as **early warning system**



Growing number of industrially produced halogenated compounds

Growing number of possible **feedstock/intermediate** products

Properties

HCFC-31

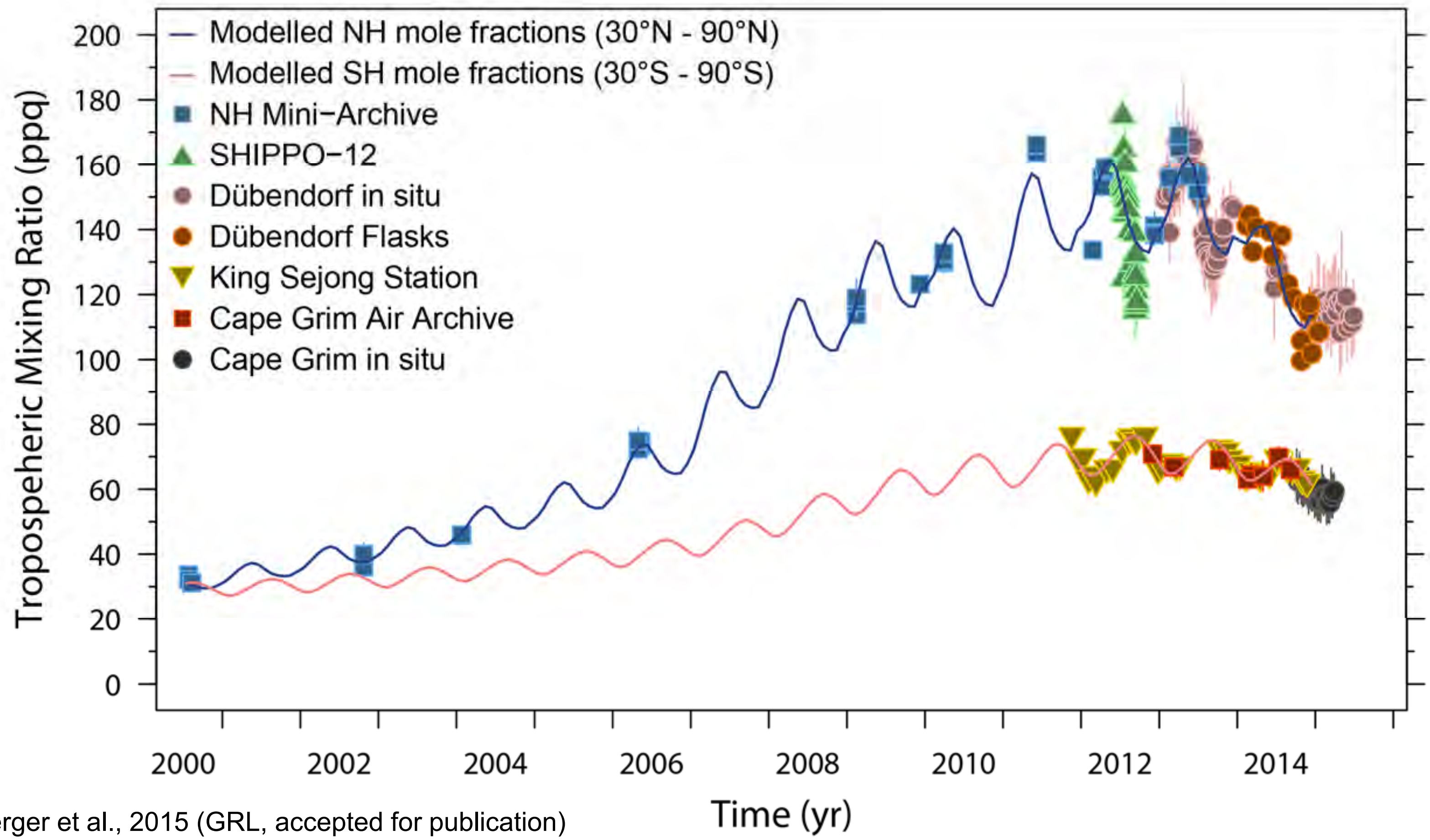
HCFC-133a

- Montreal Protocol gases with **unknown atmospheric budget**
- **Sources** not well known
- **First atmospheric measurements** of HCFC-31

(Carpenter and Reimann et al., 2014; McGillen et al., 2015)

Atmospheric History

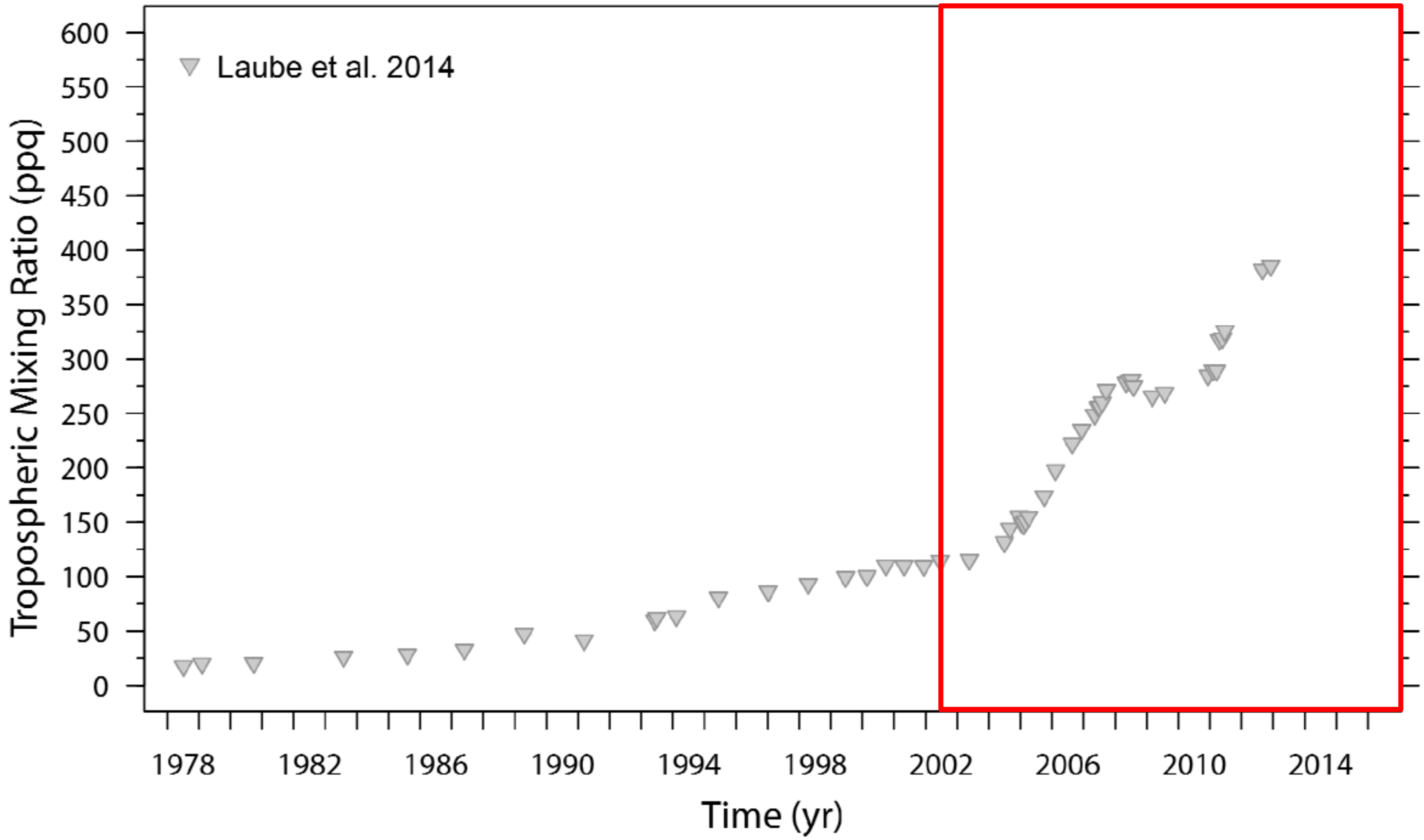
HCFC-31



Schoenenberger et al., 2015 (GRL, accepted for publication)

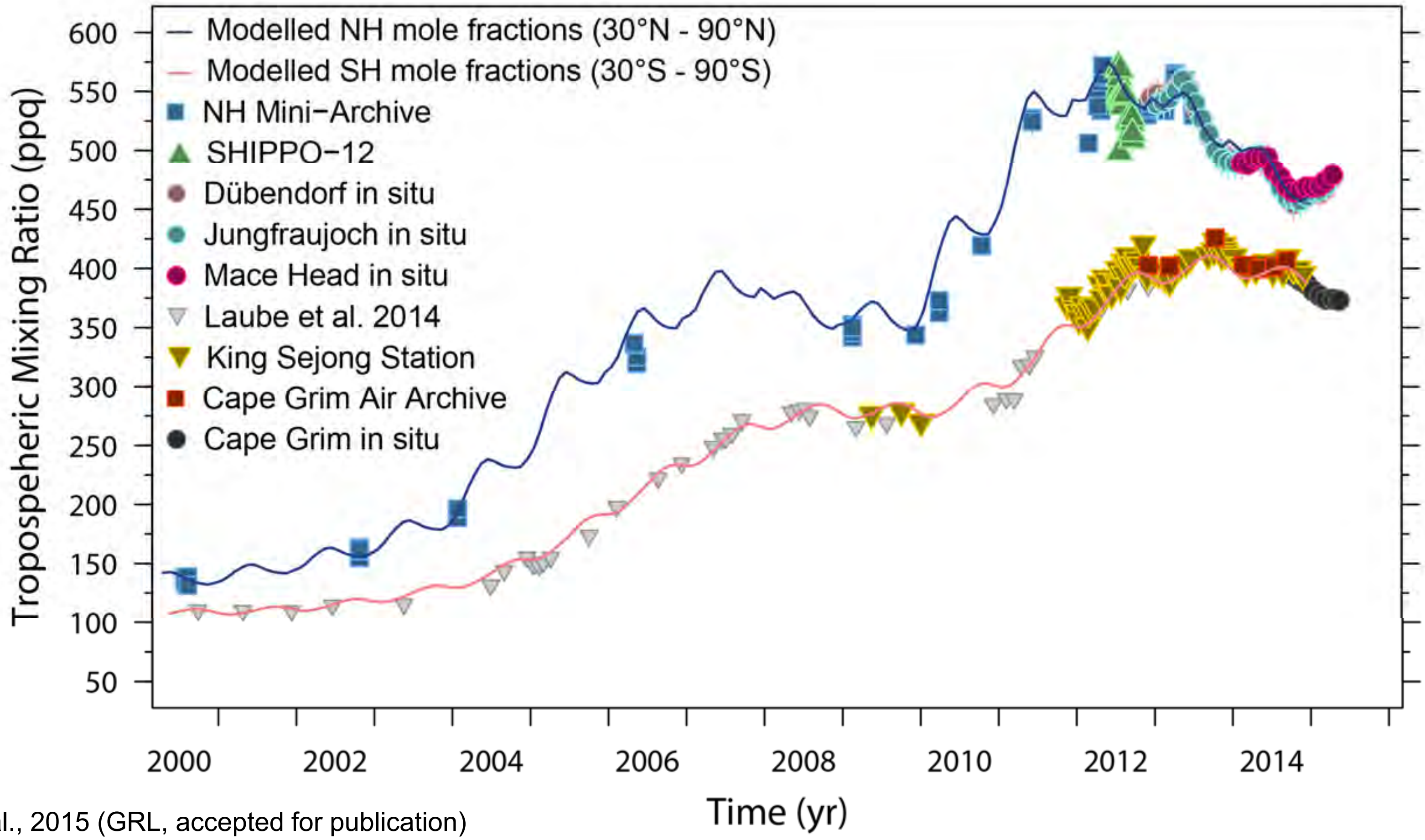
Atmospheric History

HCFC-133a



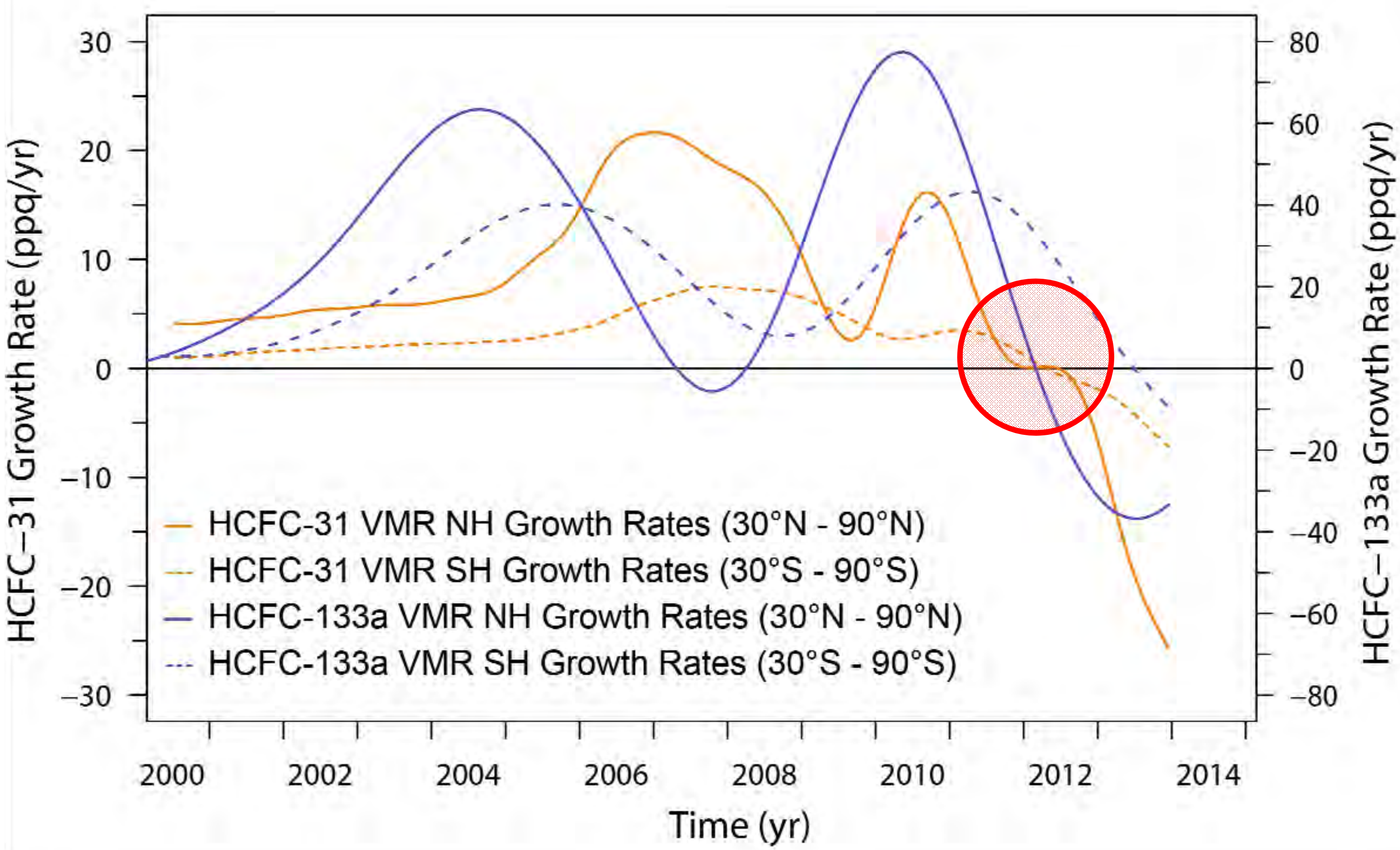
Atmospheric History

HCFC-133a



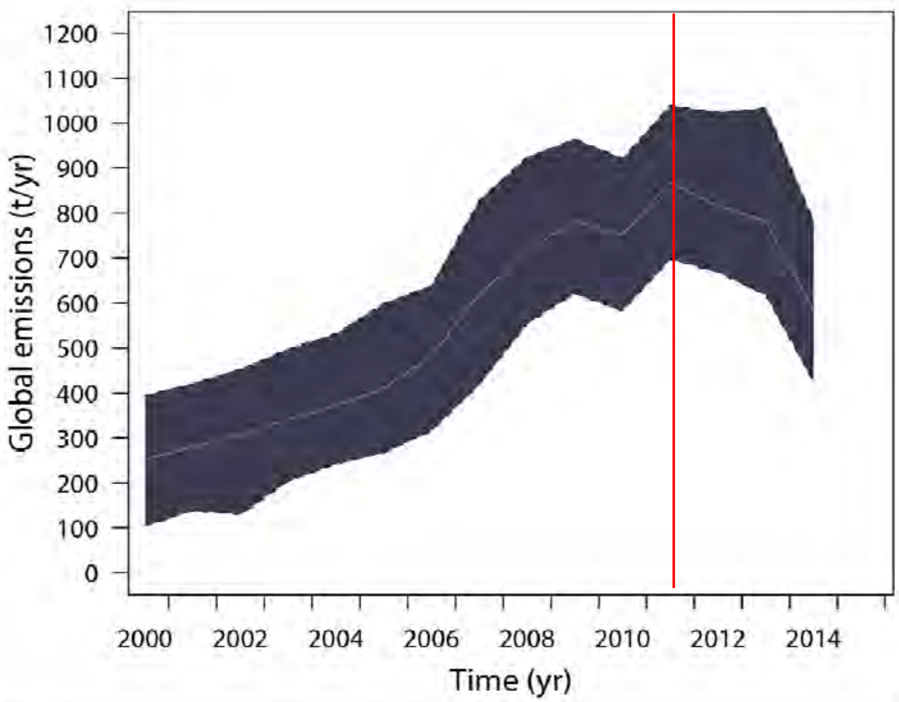
Vollmer et al., 2015 (GRL, accepted for publication)

Atmospheric History

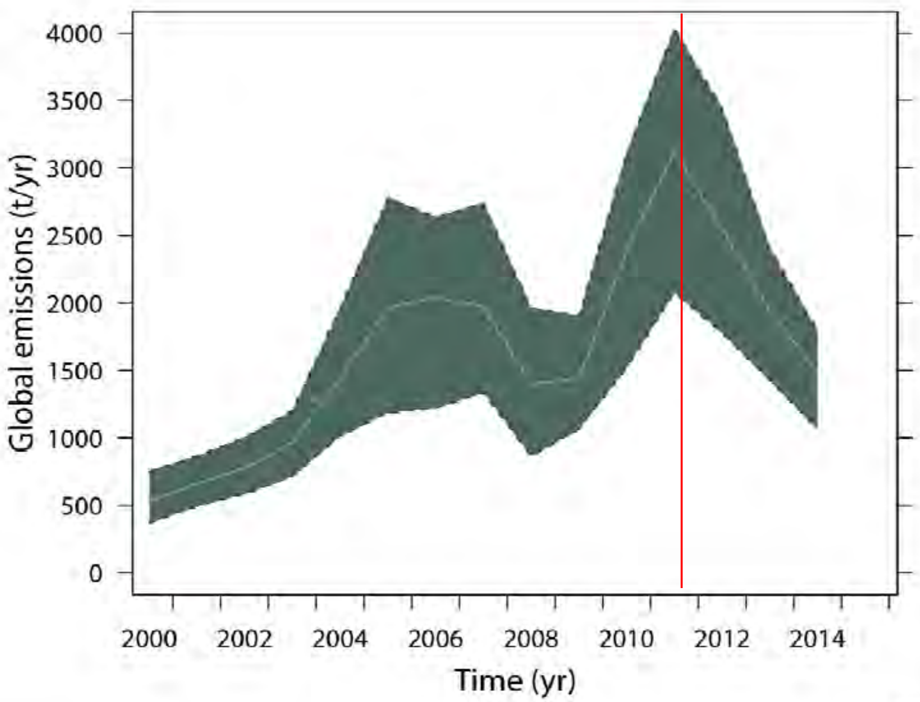


Global Emissions

HCFC-31



HCFC-133a



Modelled global emissions (AGAGE 12-box-model)

Sources

HCFC-31

HCFC-133a

Sources

HCFC-31

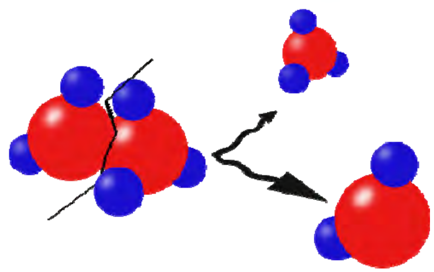
Industrial Production

HCFC-133a

Sources

HCFC-31

Degradation of CFC-11



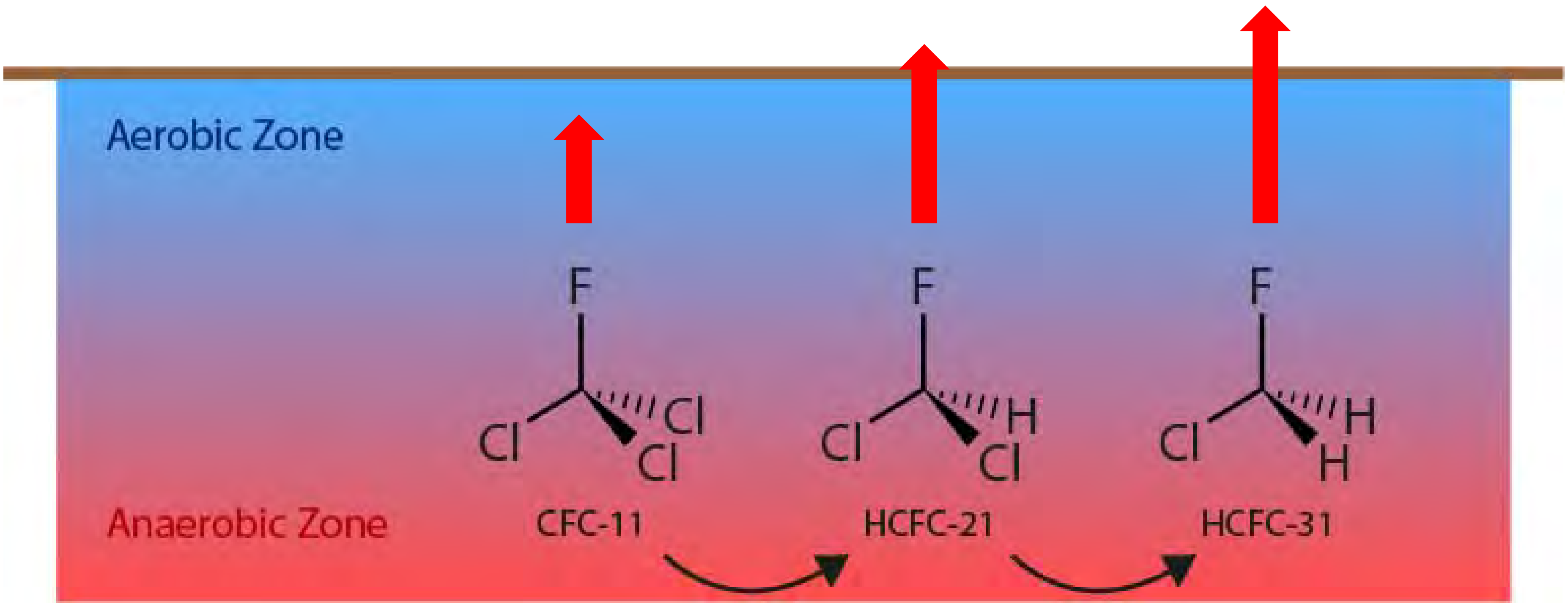
Industrial Production

Decay Product

HCFC-133a

Sources

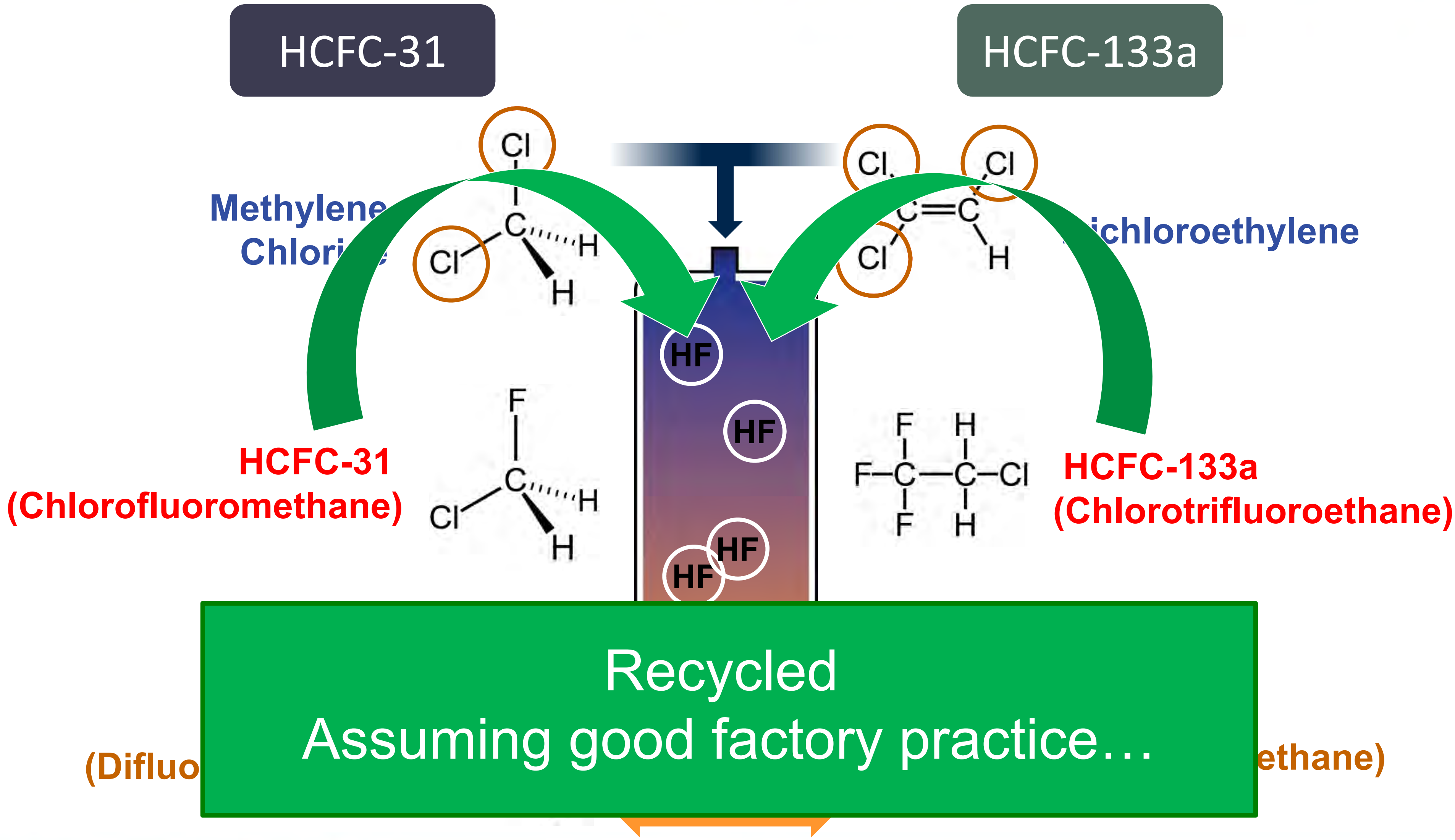
- **Degradation of CFC-11** in shredded residue landfills under anaerobic conditions by methanogenic bacteria *(Scheutz et al., 2003/2008/2012; Balsiger et al., 2005)*
- **Low emissions** of HCFC-31 detected during a field study at a Danish waste facility (Scheutz et al., 2010)



Sources

HCFC-31		HCFC-133a
	Industrial Production	
Degradation of CFC-11	Decay Product	
HFC-32	**Synthesis Intermediate**	HFC-134a

Sources



HCFC-31
HCFC-133a
Methylene
Chlori
ichloroethylene
Cl
C
H
HF
F
HCFC-31
(Chlorofluoromethane)
HCFC-133a
(Chlorotrifluoroethane)
(Difluo
ethane)
Recycled
Assuming good factory practice…

Sources

- Rapid reversal of global emissions points to source under immediate human control
  - Emissions due to poorly optimized production conditions
  - Reduction due to improvements at one or a few factories
  - Reduction of HFC-32/HFC-134a production in emitting factory

- Major HFC-32 consumption starting around 2000 in developed countries/ 2005 in developing countries (G. Velders, unpublished data)

Summary

- HCFC-31 and HCFC-133a **were rising in the atmosphere** until 2012 but declined steeply afterwards.

- **Degradation of CFC-11** can produce HCFC-31, which seems to be a **minor source** of this substance.

- **HCFC-31** is an **intermediate** during the synthesis **of HFC-32**
- **HCFC-133**a is a **intermediate** during the synthesis **of HFC-134a**

- **Industrial production and environmental degradation processes** can lead to unforeseen emissions of ozone-depleting substances.

- **Scanning the atmosphere** for new substances stays vital to serve as an **early warning system**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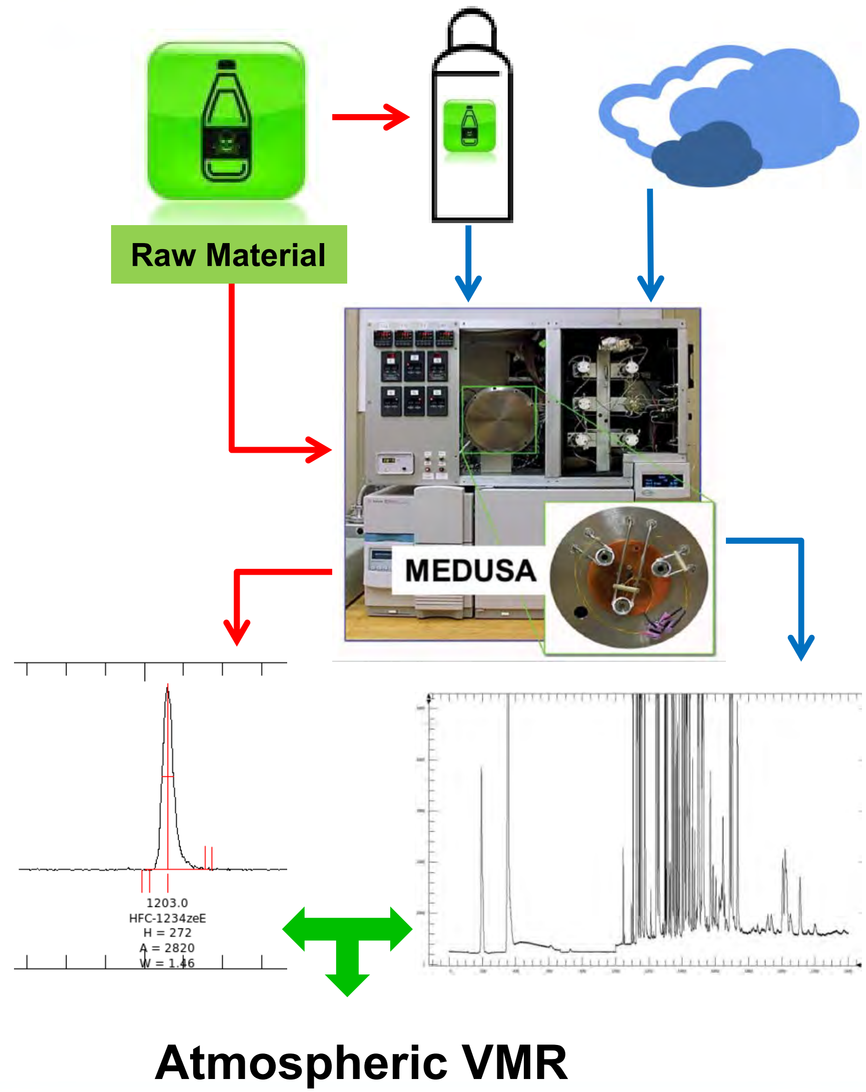
Materials Science & Technology
Thank you for your attention

[redacted]

Methods

- **Purchase raw materials**
- **Investigate chromatographic properties and mass spectra**
  - Retention Times
  - Favourable mass fragments
- **Produce standards with near ambient concentrations** (lower ppt range)
- **Instrument/Lab work**
  - stability of compounds, blanks, nonlinearities,…)
- **Measurements**



Medusa GCMS

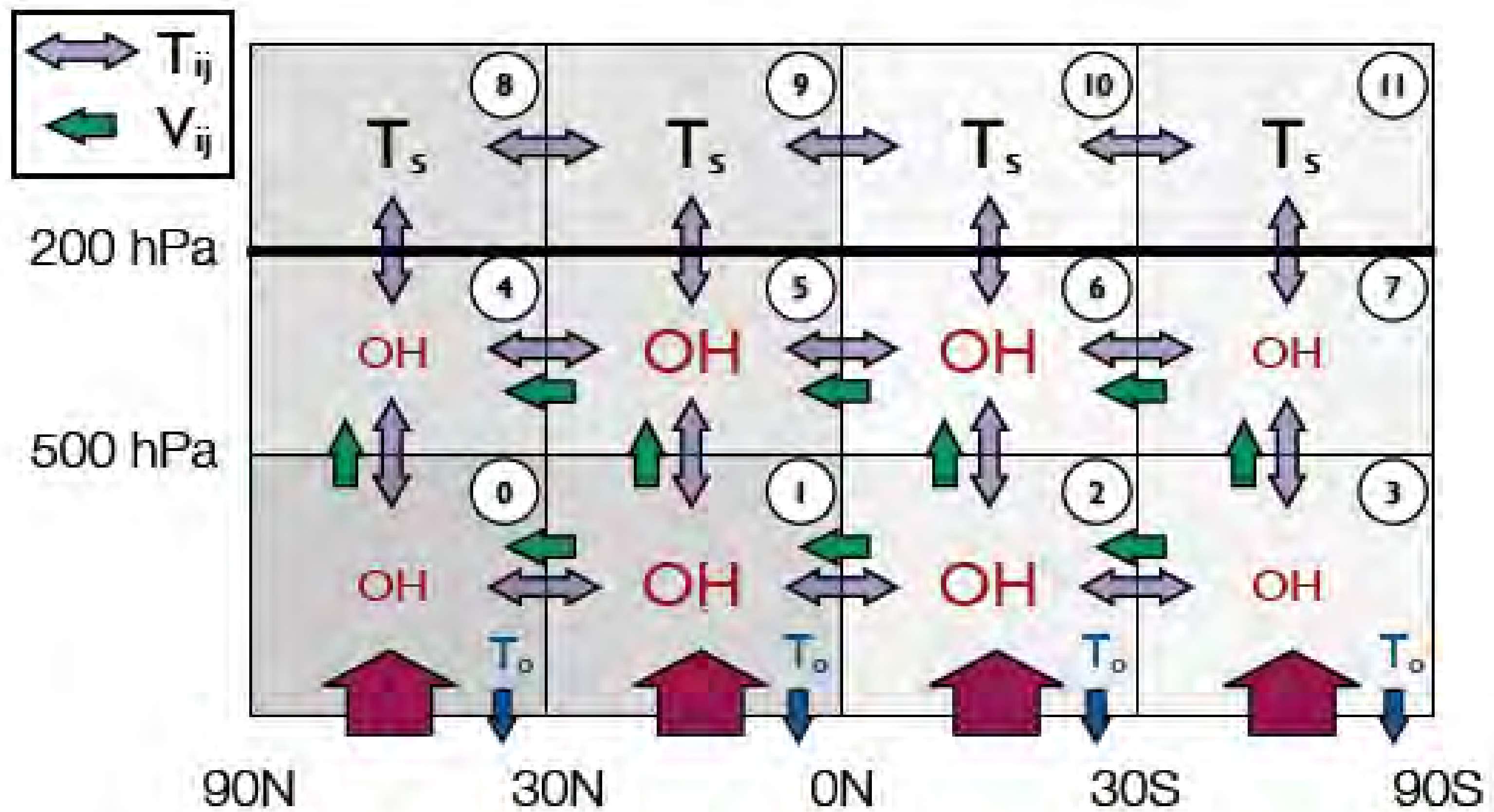
Medusa Preconcentration Unit:

- Hayesep-D packed cold traps cooled to -160°C
- Desorption at ~100°C
- Volumes:
  - Flasks generally 4L
  - In situ 2L
- Connected to:
  - Gas chromatograph (Agilent 6890N)
  - Mass spectrometer (Agilent 5975 MS)

AGAGE 12-box-model

- 4 equal-mass latitudinal sections (90°N-30°N, 30°N-0°, 0°-30°S, 30°S-90°S)
- 3 vertical layers (500 hPa, 200 hPa)
- No advection across tropopause (troposphere-stratosphere exchange determined by single mixing time-scale)
- Mixing timescales between 4 stratospheric boxes, arbitrarily set to 100 days (Cunnold, 1994)
- Emissions are assumed to be instantaneously mixed throughout the lowest boxes.
- Loss processes:
    - Instantaneous loss rate in any box (parameterizing, e.g. photolysis)
    - Reaction with OH
        - fixed OH field in the troposphere, based on monthly averages from 3D model output from Spivakovsky et al. (2000)
        - Can be adjusted in each box in the model
        - Temperatures specified in each tropospheric box, every month (NCEP/NCAR reanalysis (Kalnay et al, 1996)
    - Oceanic uptake (first-order loss timescale in the lowest box)

AGAGE 12-box-model



T_{ij} = Eddy diffusion timescales
V_{ij} = Advection rates
T_0 = parameterized oceanic/soil uptake

T_S = Instantaneous stratospheric lifetimes
OH = OH reaction rates based on seasonally varying OH levels and temperatures

AGAGE 12-box-model

Parameter	Box I	Box J	Prior (days) Winter	Spring	Summer	Fall	Optimized (days) Winter	Spring	Summer	Fall
Eddy diffusion (T_{ij}^{-1})	0	1	116	116	261	139	84	83	165	80
	1	2	495	712	363	712	244	568	187	560
	2	3	167	167	116	116	165	165	117	124
	4	5	29	35	85	52	22	26	51	40
	5	6	124	178	124	178	81	105	103	109
	6	7	52	42	29	42	60	40	31	43
	4	0	38	38	38	38	26	26	23	30
	5	1	38	38	38	38	45	39	31	38
	6	2	38	38	38	38	29	39	36	37
	7	3	38	38	38	38	31	36	37	37
	8	4	1260	1260	1260	1260	895	775	694	897
	9	5	1260	1260	1260	1260	1041	1123	1349	1198
	10	6	1260	1260	1260	1260	1645	1722	1806	1668
	11	7	1260	1260	1260	1260	1306	1688	1674	1398
	8	9	100	100	100	100	95	94	94	95
	9	10	100	100	100	100	95	95	97	96
	10	11	100	100	100	100	99	99	100	99
Advection (V_{ij})	0	1	-1506	581	1882	-442				
	1	2	-69	-376	50	126				
	2	3	1506	1075	753	1506				
	4	5	1506	-581	-1882	442				
	5	6	69	376	-50	-126				
	6	7	-1506	-1075	-753	-1506				
	4	0	-1506	581	1882	-442				
	5	1	-72	-228	52	98				
	6	2	65	279	-54	-137				
	7	3	-1506	-1075	-753	-1506				