Mise à jour sur les substances appauvrissant la couche d'ozone (SAO) et autres gaz d'intérêt pour le Protocole de Montréal

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HALOGENATED GASES

Halogenated compounds

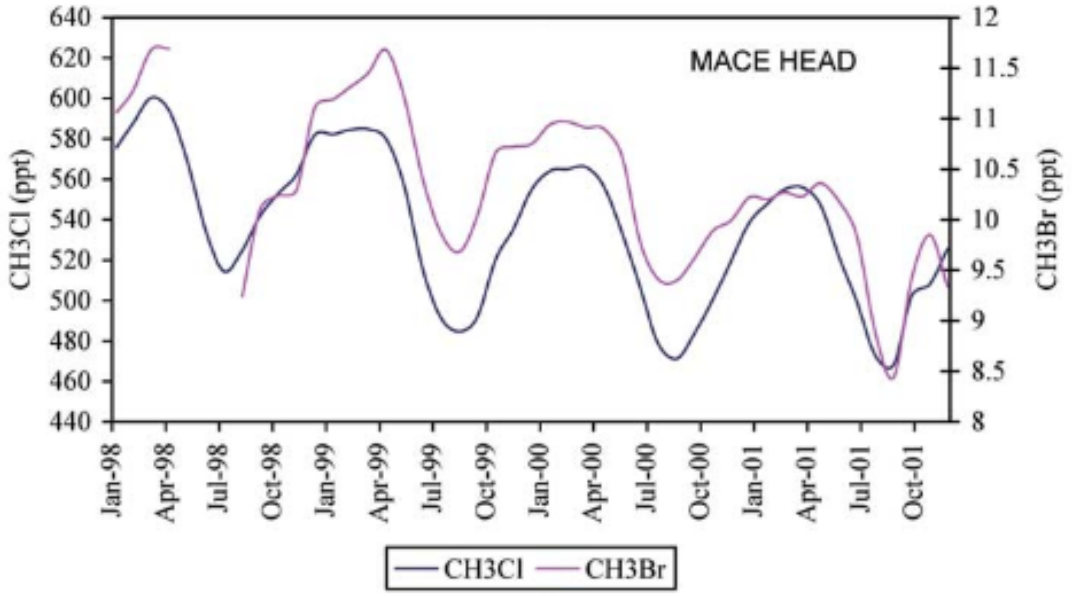
- Organic compounds carrying F, Cl, Br, I*, mono-, poly- or per-halogenated...
- The range of halogenated compounds present in the troposphere has been considerably modified over the last few decades as a result of the intensive use of numerous synthetic products in extremely diversified applications, massively emitted to the atmosphere after use
- Mainly derived from alkanes (C_nH_{2n+2}) $\Rightarrow$ organic chlorine
- But also SF_6, SF_5CF_3
- Targeted by the Montreal (Cl and Br) and/or Kyoto (F) Protocols
- Fluorinated or per-fluorinated ethers (ROR', HFEs), which are currently not subject to any regulation, although some of them have long lifetimes and high GWPs (see Table A-5 in WMO2022**)

(*) We will not address here iodine compounds (CH_3I, CH_2I_2...), their lifetime is of the order of one hour to a few days, they are present in very small quantities in the Earth's atmosphere.

(**) Scientific Assessment of ozone depletion of the World Meteorological Organization (WMO), 2022 [https://hdl.handle.net/2268/299913].

Methyl chloride (CH_3Cl)

- CH_3Cl is the most abundant halogen compound in the Earth's atmosphere (troposphere), with an average mixing ratio of 545 ppt (WMO, 2022)
- It has no long-term trend, although significant interannual variations are observed (e.g., in relation to intense forest fires)
- It has natural sources (tropical and sub-tropical plants, oceans, biomass combustion...) and anthropogenic sources (industrial processes, domestic wood heating...)
- The main sink is the destruction by OH, in the troposphere
- In imbalance (sinks exceed sources), its atmospheric budget (Table 1-4, WMO, 2014) is still subject to high uncertainties, so it is not excluded that significant sources and/or sinks have not yet been identified or properly assessed; industrial sources located in China could compensate for this imbalance (section 1.2.6. in WMO, 2018)
- CH_3Cl has a lifetime of 0.9 year and a global warming potential (GWP; over 100 years) of 6
- Given this relatively short lifetime, there are marked latitudinal and seasonal variations



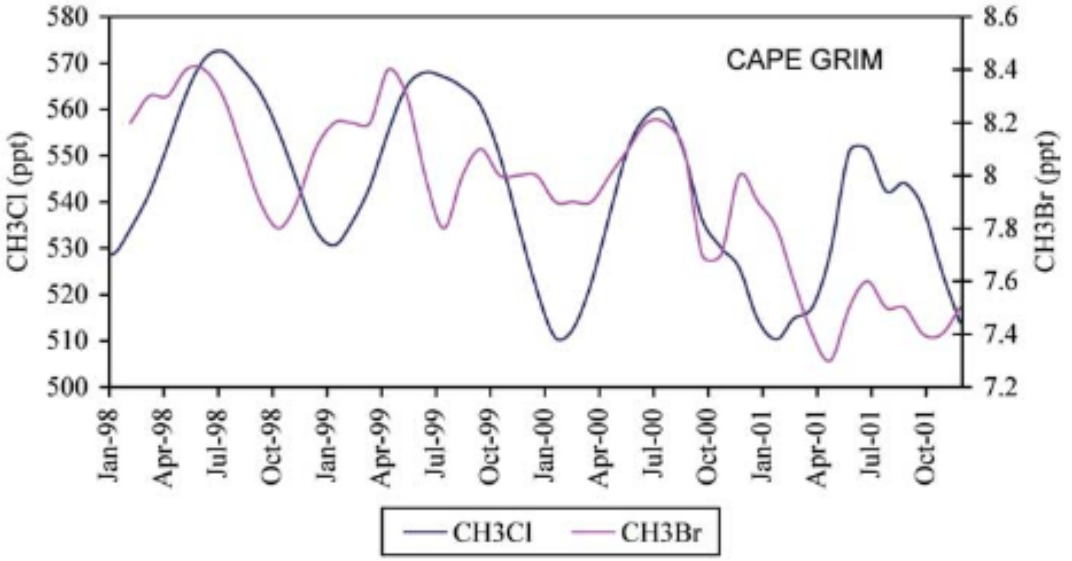


Figure 3. Baseline monthly mean mole fractions of CH_3Br and CH_3Cl determined at the Mace Head and Cape Grim AGAGE stations, (1998–2001).

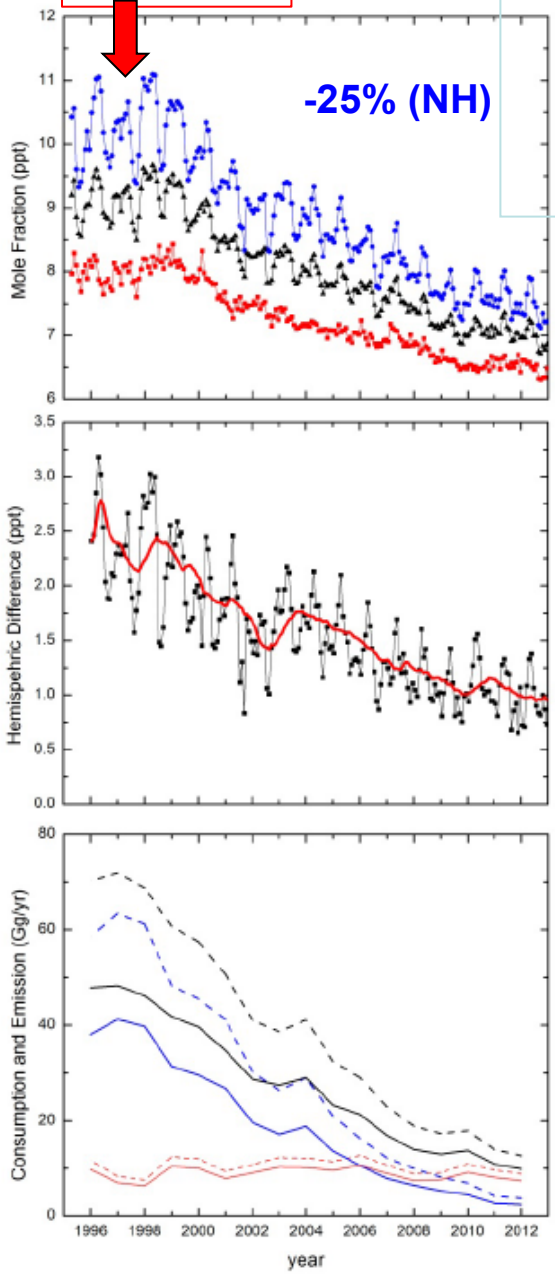
After Simmonds et al. *J. Atmos. Chem.*, **47**, 2004.

Surface *in situ* mesurements performed at two AGAGE sites:

- Mace Head, Ireland, 54°N
- Cape Grim, Tasmania, 41°S
- No marked trend: declining between 2008 and 2011, increasing between 2011 and 2016 (WMO, 2014, 2018)

CH_3Br is the most abundant brominated compound. It has both natural and anthropogenic sources and is regulated by the Montreal Protocol. It has a short lifetime and a GWP of 2

CH_3Br : declining



WMO, 2011, 2014, 2018

Table 1-2. Summary of the estimated source and sink strengths (Gg/yr) of methyl bromide (CH_3Br) for periods 1996–1998 and 2008.

	1996–1998	Range	2008	Range	Reference	Note
SOURCES						
Fumigation- dispersive (soils)	41.5	(28.1 to 55.6)	6.7	(4.6 to 9.0)	1, 2	a
Fumigation- quarantine/ pre-shipment	7.9	(7.4 to 8.5)	7.6	(7.1 to 8.1)	1, 2	b
Ocean	42	(34 to 49)	42	(34 to 49)	3, 4	c
Biomass Burning	29	(10 to 40)	29	(10 to 40)	5, 6	d
Leaded gasoline	5.7	(4.0 to 7.4)	<5.7		7	e
Temperate peatlands*	0.6	(−0.1 to 1.3)	0.6	(−0.1 to 1.3)	8, 9, 10	f
Rice paddies*	0.7	(0.1 to 1.7)	0.7	(0.1 to 1.7)	11, 12	g
Coastal salt marshes*	7	(0.6 to 14)	7	(0.6 to 14)		h
based on California saltmarshes	14	(7 to 29)	14	(7 to 29)	13, 14	i
based on Scottish saltmarsh	1	(0.5 to 3.0)	1	(0.5 to 3.0)	15	j
based on Tasmania saltmarsh	0.6	(0.2 to 1.0)	0.6	(0.2 to 1.0)	16	k
Mangroves	1.3	(1.2 to 1.3)	1.3	(1.2 to 1.3)	17	l
Shrublands*	0.2	(0 to 1)	0.2	(0 to 1)	18	m
Rapeseed	4.9	(3.8 to 5.8)	5.1	(4.0 to 6.1)	19	n
Fungus (litter decay)	1.7	(0.5 to 5.2)	1.7	(0.5 to 5.2)	20	o
Fungus (leaf-cutter ants)	0.5		0.5		21	p
Potential terrestrial sources						q
Tropical trees	n.q.		n.q.		22, 23	r
Temperate woodlands	n.q.		n.q.		24, 25	s
Tropical ferns	n.q.		n.q.		26	
Abiotic decomposition	n.q.		n.q.		27	t
Subtotal (Sources)	**143**		**111.5**			
SINKS						
Ocean	56	(49 to 64)	49	(45 to 52)	3	u
OH and photolysis	77		63.6		3	v
Soils	40	(23 to 56)	32	(19 to 44)	28–33	w
Subtotal (Sinks)	**177**		**147.6**			
Total (SOURCES−SINKS)	**−34**		**−36.1**			

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Methyl bromide (CH_3Br)*: now stabilized

- Methyl bromide is the shortest-lived of the substances controlled by the Montreal Protocol and has natural and anthropogenic sources
- Eliminating future emissions of methyl bromide (CH_3Br) from quarantine and pre-shipment applications currently allowed by the Montreal Protocol would accelerate the return of mid-latitude equivalent stratospheric chlorine to 1980 abundances by two years
- Methyl bromide (CH_3Br) abundances have varied annually between 6.5 ppt and 6.9 ppt during 2016–2020 with no clear overall trend
- Most anthropogenically produced CH_3Br has been phased out except for quarantine and pre-shipment fumigation, leaving natural emissions as the dominant source
- Reported quarantine and pre-shipment consumption has been relatively stable for more than two decades

*WMO2022 update

Chlorofluorocarbons (CFC)

- Synthetic products discovered in the 1930s; no natural source identified
- Per-halogenated saturated carbon compounds containing Cl and F simultaneously
- General chemical formula: $C_nCl_mF_q$ where m+q = (2n+2)
- With extremely interesting physical and thermodynamic properties: non-toxic, non-flammable, stable, odorless, used in many industrial and domestic applications.
- Low production costs
- $\Rightarrow$ Very large quantities of CFCs - especially CFC-12 (CCl_2F_2) and CFC-11 (CCl_3F) - have been produced by the chemical industry since the 1950s.
- They have been used as propellant agents (aerosol cans), in refrigeration and air conditioning systems (refrigerant fluids), as blowing agents for foam expansion (construction, refrigerators, etc) and packaging, for cleaning electronic components (CFC-113, CCl_2FCClF_2) during assembly, etc.

Chlorofluorocarbons (CFC)

Awareness of the environmental threat posed by these miracle products, three key steps :

- In 1973, Lovelock showed that CFC-11 is present at a global scale at a level of 60 pptv. However, its sources are mainly located in the northern hemisphere. Moreover, the comparison of emission inventories and concentrations demonstrates the very high stability of this product in the atmosphere
- In 1974, *Molina and Rowland* as well as *Stolarski and Cicerone* almost simultaneously put forward the hypothesis that the photolysis of CFCs in the stratosphere would lead to the release of Cl atoms capable of destroying ozone according to the ClO_x cycle
- The concerns raised by this work were reinforced by Farman's observations, which highlighted the "ozone hole" over the Antarctic in the spring of 1984

Apart from being threatening gases to ozone, the CFCs have strong IR absorptions combined with long lifetimes. They are therefore powerful GHGs with very high GWPs (6410 and 12500 resp. for CFC-11 and -12, 100-year horizon, WMO2022). Their accumulation in the atmosphere since 1950s has significantly contributed to radiative forcing (RF; 8% of the GHG contribution between 1750 and 2021; WMO Greenhouse Gas Bulletin n°18, 2022)

Chlorofluorocarbons (CFC)

- Degradation in the stratosphere (CFC-11) :

  $CCl_3F + h\nu \rightarrow CCl_2F + Cl$

  $CCl_2F + O_2 + M \rightarrow CCl_2FO_2 + M$

  $CCl_2FO_2 + NO \rightarrow CCl_2FO + NO_2$

  $CCl_2FO + M \rightarrow COClF + Cl$ (loss of 2 Cl)

- Similarly (CFC-12) :

  $CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl$

  $CClF_2 + O_2 + M \rightarrow CClF_2O_2 + M$

  $CClF_2O_2 + NO \rightarrow CClF_2O + NO_2$

  $CClF_2O + M \rightarrow COF_2 + Cl$ (loss of 2 Cl)

- C-Cl bonds break before C-F bonds, the more F atoms these molecules bear, the more stable the CFCs will be
- COClF is a fairly stable reservoir of Cl and F, its subsequent destruction will release a third atom of Cl
- COF_2 is the second largest reservoir of F in the stratosphere, after hydrogen fluoride (HF)
- Their oxidation by $O(^1D)$ must also be accounted for

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$O_3 + O \rightarrow 2\,O_2$$

Hydrochlorofluorocarbons (HCFC)

- The gradual ban on CFCs has forced manufacturers to develop substitutes that are less harmful to the ozone layer
- HCFCs were the first substitutes to be introduced; they have at least one C-H bond and generally bear fewer Cl atoms than the CFCs.
- The C-H bond is sensitive to OH oxidation in the troposphere, thus limiting the fraction of HCFCs that can reach the stratosphere
- Destruction by OH following:

  $C_nX_{2n+1}H + OH \rightarrow H_2O + \bullet CX_{2n+1}$ where X stands for H, F or Cl

  This destruction continues according to the reaction scheme indicated before for the methane oxidation
- The industrial and domestic applications of these products are logically very similar to those of CFCs
- The main HCFCs are HCFC-22 ($CHClF_2$), HCFC-142b (CH_3CClF_2) and HCFC-141b (CH_3CCl_2F), with GWPs of 1910, 2190 and 808 respectively (WMO2022)
- Currently close to stabilization, the contribution of HCFCs to RF will likely remain moderate (estimated at 2% between 1750 and 2021, which is ~4 times less than that of CFCs)

Hydrofluorocarbons (HFC)

- Other/next substitutes for CFCs, with properties and applications very similar to HCFCs
- Their growth was initially limited by their higher manufacturing costs compared to those of CFCs and HCFCs, it is now booming
- They are harmless to ozone.
- HFC-134a (CH_2FCF_3) and HFC-23 (CHF_3) are the most abundant in the atmosphere
- The GWPs of these HFCs are 1470 and 14700 respectively (WMO2022)
- Their current contribution to the RF recently reached 1%

CH_3CCl_3 & CCl_4

- Industrial compounds, chlorinated alkane derivatives which have been used in very large quantities as cleaning solvents (CH_3CCl_3, methyl chloroform or trichloroethane) or as a reactant in the synthesis of CFC-11 and -12 (CCl_4, carbon tetrachloride)
- Significant contributions to the chlorine budget in the atmosphere
- Marginal contribution to the RF, decreasing due to the decrease in their atmospheric concentrations

But…

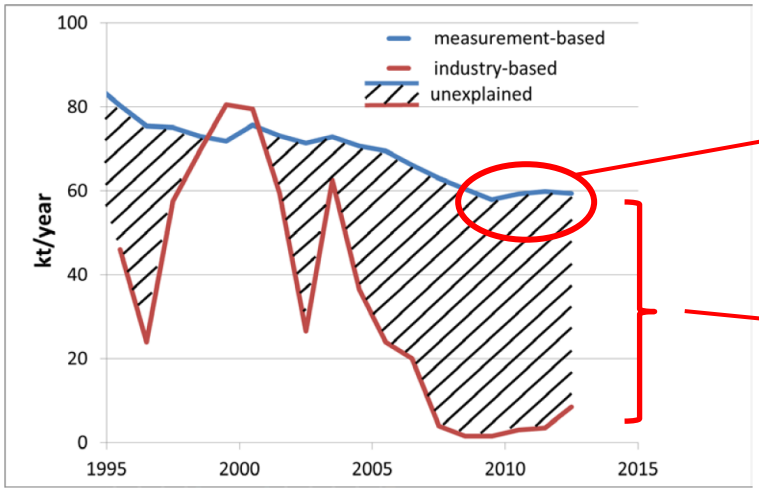
- The scientific community questioned the "too slow" decline of CCl_4
- It is not possible to reconcile "top-down" emissions with "bottom-up" emission inventories based on industry data
- In addition, capture by sinks were affected by significant uncertainties
- The inter-hemispheric gradient (HN-HS =1.5±0.2 ppt for 2000-2012) suggests significant emissions for the most populated regions

CCl_4 in the WMO/UNEP Ozone Assessment 2014

Total atmospheric lifetime of CCl_4 = 26 years

44 years stratosphere + 94 years ocean + 195 years soil

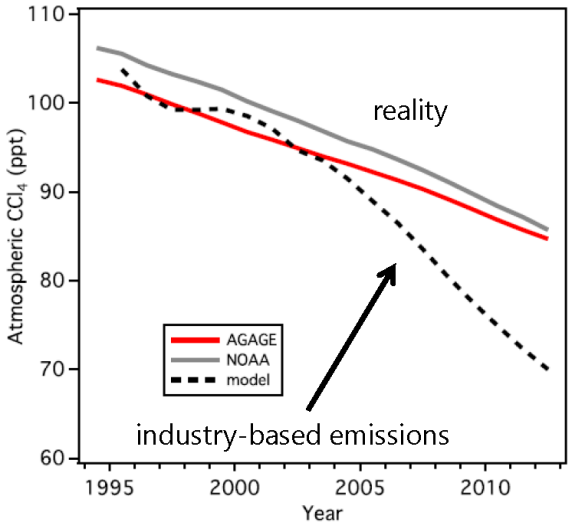
Emissions



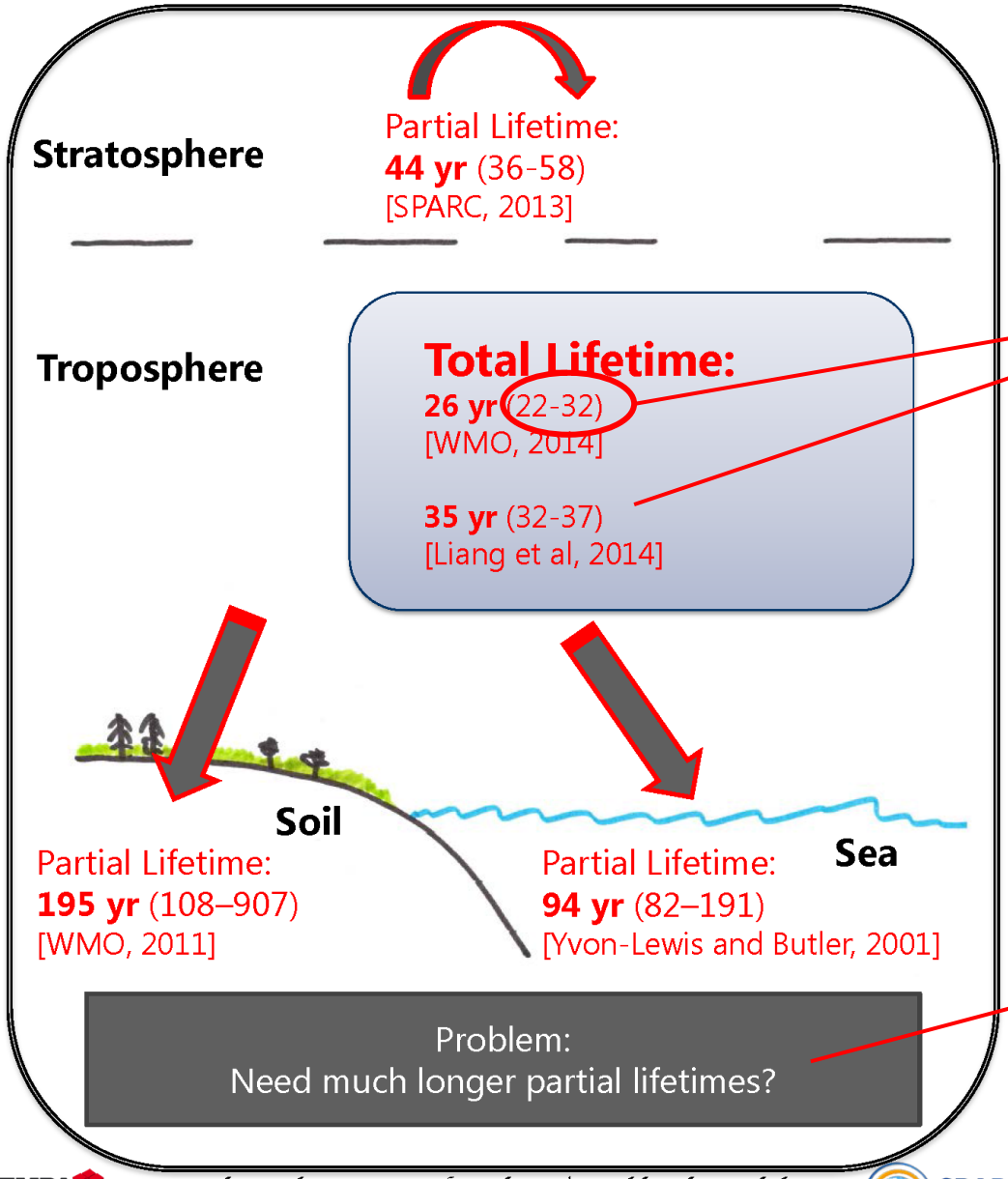
The emissions would be slightly on the rise

The difference has been significant since the mid-2000s and correspond to about 1600 tank wagons filled with liquid CCl_4

Atmospheric burden



Sinks: another poorly known parameter



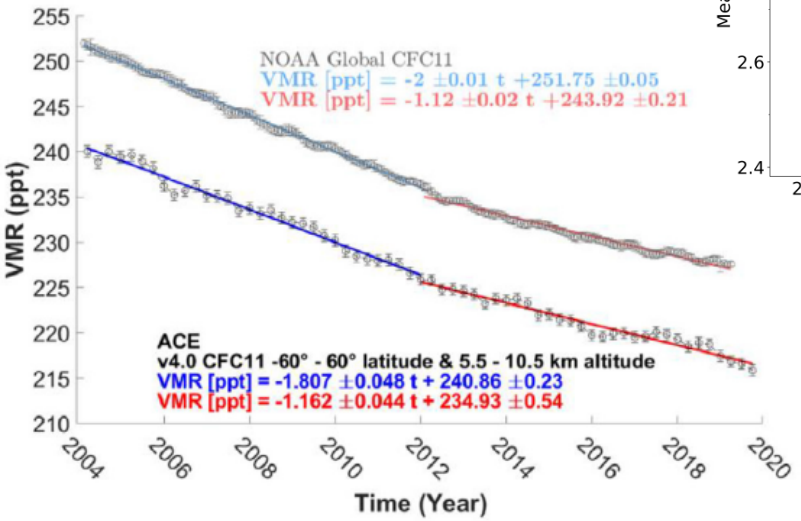
Uncertainties on global and partial lifetimes were significant

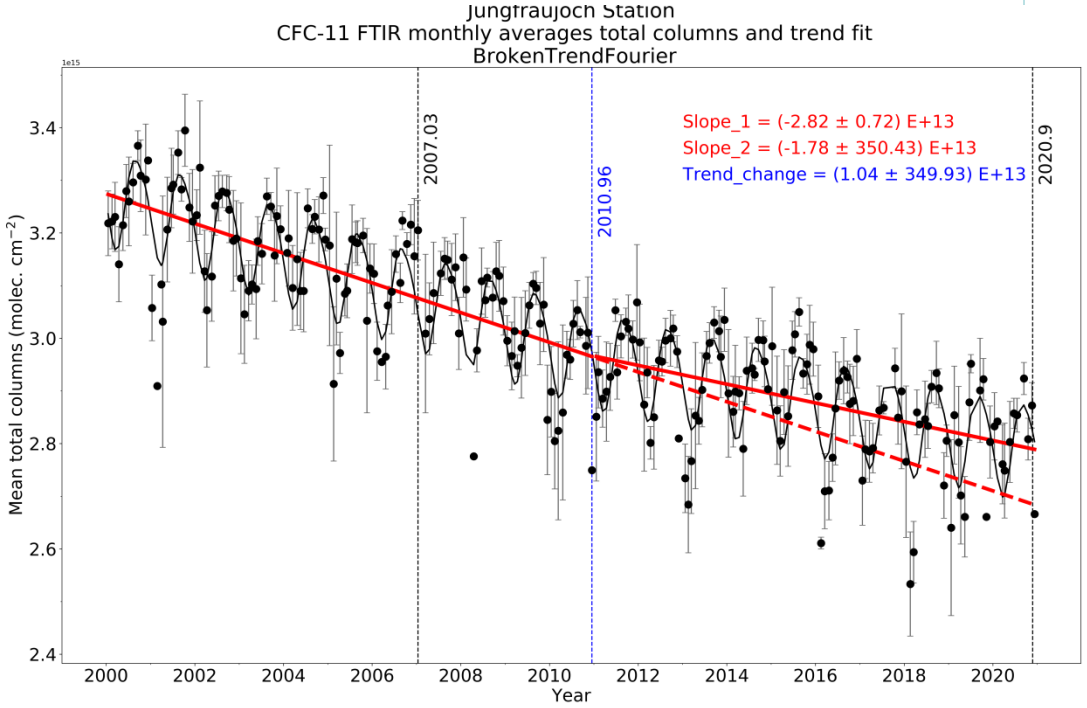
However, partial lifetimes would have to be much longer to justify a global lifetime allowing to reconcile inventories and observations.

CCl_4: the WMO2022 update

- The evaluation of the partial lifetime wrt the ocean sink has been improved (124 yr in the 110-150 yr range): better lifetime estimate => better evaluation of the emissions
- The rate at which CCl_4 has declined in the atmosphere remains slower than expected from its reported use as a feedstock (for the production of other chemicals) and its removal rate from the atmosphere
- Emissions have recently been stable at 44 ± 15 Gg/yr for 2016 and 2020

CFC-11: other evidences…





Pardo Cantos et al. (2022)

Figure: Trends for ACE-FTS and from Montzka et al., 2018. Source: Bernath et al., 2020. Slowdown in the decrease of CFC-11 atmospheric concentrations.

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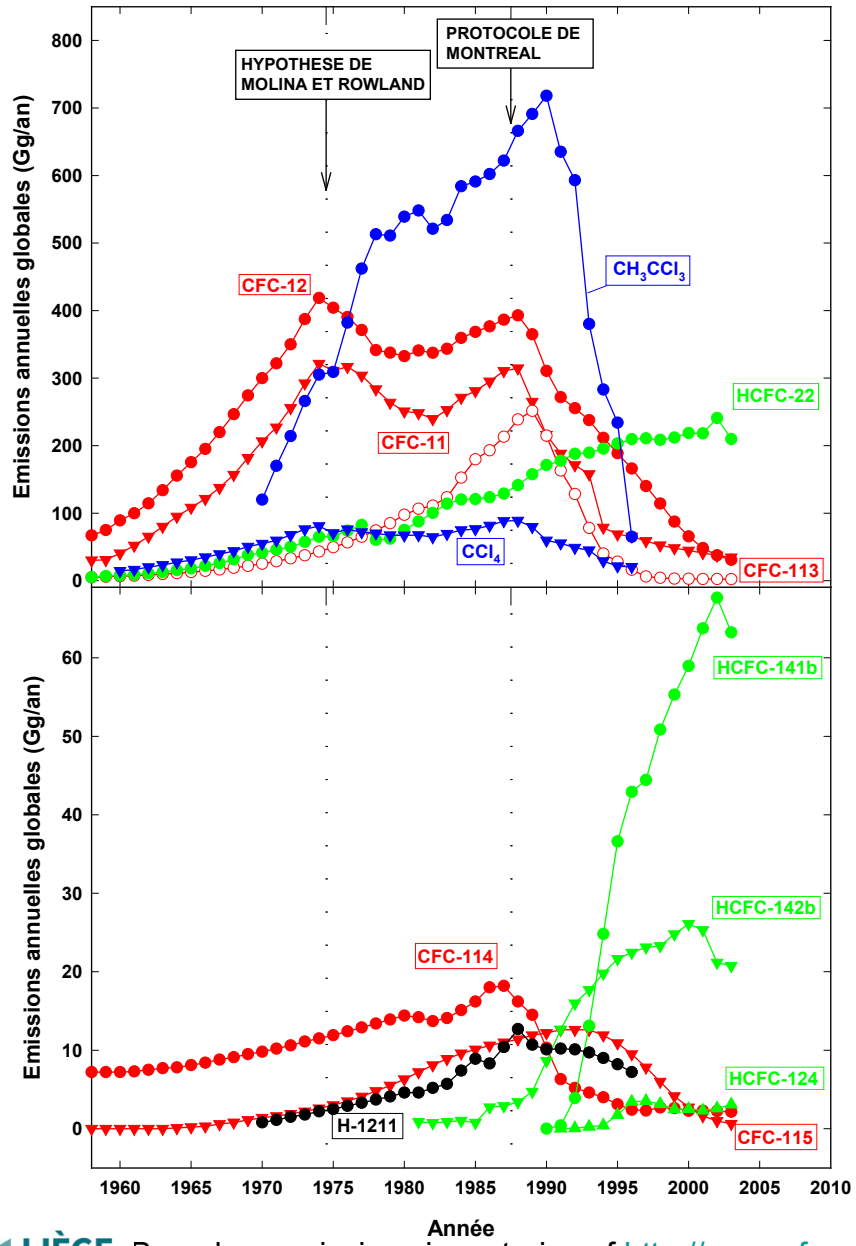
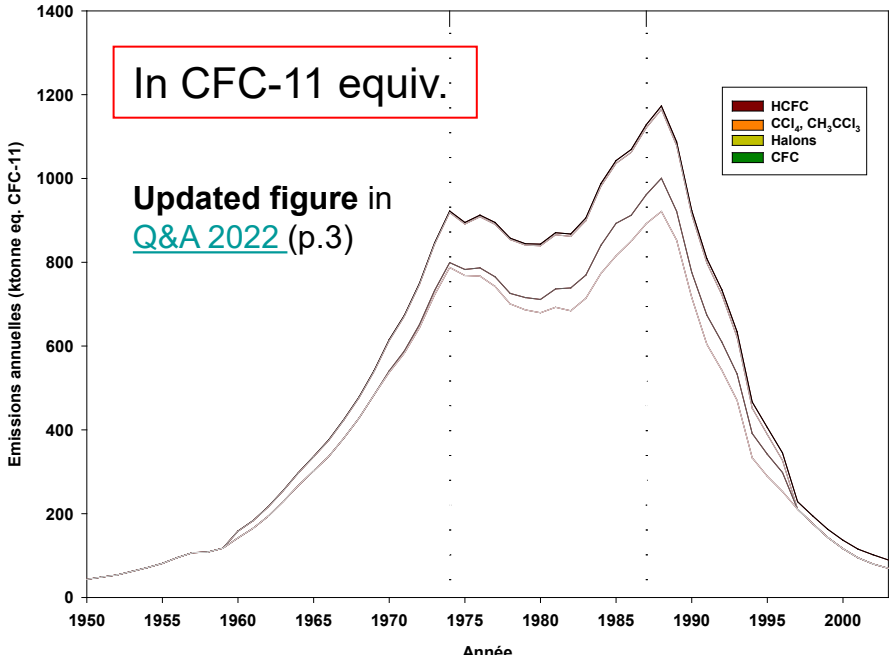
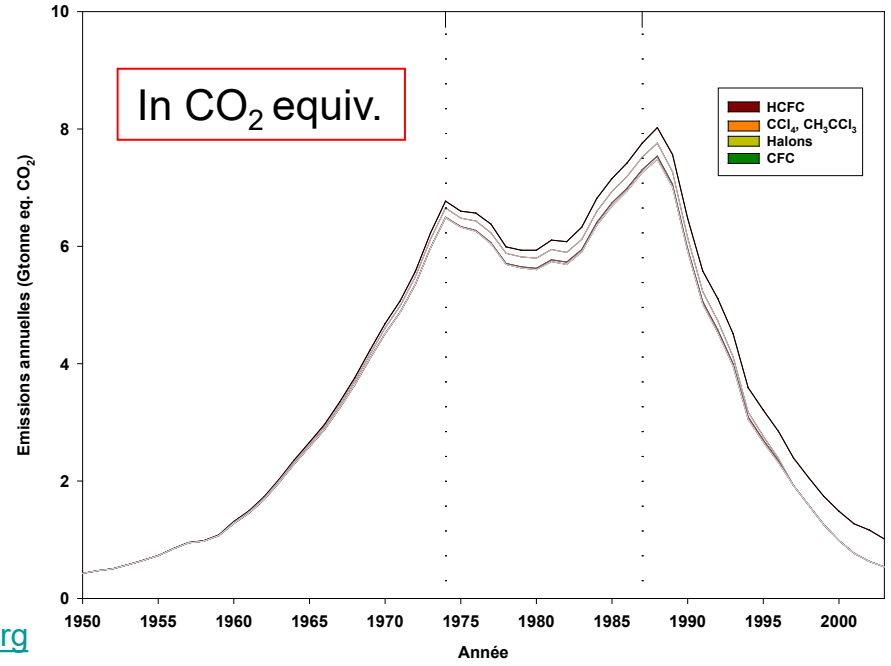
PFC et SF_6

- PFCs : mostly CF_4 and C_2F_6
- These two compounds are formed during the electrolytic production of aluminum (anode effect, the fluorine salts present in the electrolytic bath combine with the carbon anodes when the quantity of mineral (alumina; Al_2O_3) decreases: $4F^- + C \rightarrow CF_4$); this is the main anthropogenic source of CF_4
- The most modern production plants make it possible to limit or even eradicate this phenomenon. Both emission inventories and the temporal analysis of the atmospheric accumulation of CF_4 indicate that its emissions are decreasing (from 16 to 12 Gg/year between the end of the 1980s and the 1990s) despite an increase in aluminum production
- Natural sources of CF_4 would have contributed for almost half of its current atmospheric content (~35/80, process of degassing of the Earth's crust containing fluorinated minerals)
- Current concentrations of C_2F_6 (~3ppt) are consistent with emissions from aluminum production; no natural sources have been identified to date
- SF_6 is the most efficient GHG (GWP 24700), of purely anthropogenic origin, its concentration has been multiplied by 200 between 1970 and today, it is mainly used as insulating fluid in high voltage transformers
- Even if the contribution of these gases to RF remains low, their emissions should be limited as much as possible given their extremely long lifetimes, ranging from ~1,000 to 50,000 years

Emissions of halogenated compounds







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Based on emissions inventories of http://www.afeas.org

Recent changes in the concentrations of a suite of halogenated compounds

WMO, 2022

Chemical	Mole Fraction (ppt)		Change (2019–2020)		Emissions (Gg yr^{-1})		CO_2-eq. Emissions (Tg yr^{-1})	Network
	2016	2020	(ppt yr^{-1})	(% yr^{-1})	2016	2020	2020	
CFCs								
CCl_3F (CFC-11)	229.4	223.8	−2.2	−1.0	67 ± 10	48 ± 10	310 ± 64	AGAGE[1]
	230.0	224.0	−2.5	−1.1	77 ± 10	46 ± 10	298 ± 62	NOAA[2]
	230.0	225.5	−2.0	−0.9	n.a.	n.a.	n.a.	UCI
CCl_2F_2 (CFC-12)	514.5	500.7	−3.9	−0.8	30 ± 21	27 ± 21	334 ± 268	AGAGE
	511.9	497.2	−4.2	−0.8	36 ± 21	23 ± 20	282 ± 252	NOAA
	515.6	504.7	−3.7	−0.7	n.a.	n.a.	n.a.	UCI
$CClF_3$ (CFC-13)	3.18	3.32	0.04	1.1	0.5 ± 0.2	0.6 ± 0.2	10 ± 3	AGAGE
CCl_2FCCl_2F (CFC-112)	*0.42*	*0.39*	*−0.01*	*−1.8*	*n.a.*	*n.a.*	*n.a.*	UEA/FZJ
CCl_2FCClF_2 (CFC-113)	71.5	69.4	−0.5	−0.7	6.5 ± 6.4	6.9 ± 6.0	45 ± 39	AGAGE
	71.5	68.9	−0.7	−1.0	5.5 ± 5.0	6.4 ± 4.8	42 ± 32	NOAA
	71.1	70.0	−1.1	−1.6	n.a.	n.a.	n.a.	UCI
CCl_3CF_3 (CFC-113a)	*0.66*	*0.94*	*0.09*	*10*	*n.a.*	*n.a.*	*n.a.*	UEA/FZJ
$CClF_2CClF_2$ (CFC-114)	16.28	16.28	−0.01	−0.03	2.3 ± 0.9	2.6 ± 0.9	24 ± 8	AGAGE[3]
	14.64	*14.68*	*0.03*	*0.2*	*n.a.*	*n.a.*	*n.a.*	UEA/FZJ[4]
CCl_2FCF_3 (CFC-114a)	*1.04*	*1.11*	*0.02*	*1.7*	*n.a.*	*n.a.*	*n.a.*	UEA/FZJ[4]
$CClF_2CF_3$ (CFC-115)	8.50	8.71	0.03	0.4	1.5 ± 0.5	1.0 ± 0.6	10 ± 5	AGAGE
	8.62	*8.86*	*−0.02*	*−0.2*	*n.a.*	*n.a.*	*n.a.*	NIES
HCFCs								
$CHClF_2$ (HCFC-22)	237.5	248.0	1.3	0.5	375 ± 53	348 ± 55	664 ± 104	AGAGE
	237.4	247.8	1.0	0.4	373 ± 51	337 ± 53	643 ± 102	NOAA
	242.3	256.1	3.3	3.1	n.a.	n.a.	n.a.	UCI
CH_3CCl_2F (HCFC-141b)	24.49	24.52	0.14	0.58	60 ± 9	58 ± 9	47 ± 7	AGAGE
	24.53	24.50	0.12	0.5	62 ± 8	56 ± 8	45 ± 7	NOAA
	24.6	25.8	−0.2	−0.8	n.a.	n.a.	n.a.	UCI
CH_3CClF_2 (HCFC-142b)	22.54	22.23	−0.23	−1.0	24 ± 4	19 ± 4	41 ± 10	AGAGE
	22.02	21.69	−0.26	−1.2	25 ± 4	19 ± 4	41 ± 10	NOAA
	23.2	22.8	0.00	0.0	n.a.	n.a.	n.a.	UCI
Chlorocarbons								
CH_3Cl (methyl chloride)	553.6	545.5	3.3	0.6	4699 ± 960	4720 ± 946	28 ± 6	AGAGE
	559.3	549.4	3.0	0.6	4756 ± 975	4718 ± 959	28 ± 6	NOAA
CCl_4 (carbon tetrachloride)	79.92	76.34	−1.01	−1.3	42 ± 15	41 ± 14	89 ± 30	AGAGE
	81.31	77.10	−1.32	−1.7	45 ± 15	46 ± 14	99 ± 31	NOAA
	81.9	77.4	−0.3	−0.4	n.a.	n.a.	n.a.	UCI
CH_3CCl_3 (methyl chloroform)	2.62	1.42	−0.23	−14	2.2 ± 2.0	2.3 ± 1.1	0.4 ± 0.2	AGAGE
	2.60	1.40	−0.22	−14	2.9 ± 1.8	2.2 ± 1.0	0.4 ± 0.2	NOAA
	3.05	1.47	−0.26	−15	n.a.	n.a.	n.a.	UCI

Decreasing

levelling off

Strong decline for CH_3CCl_3 (22 ppt in 2004)

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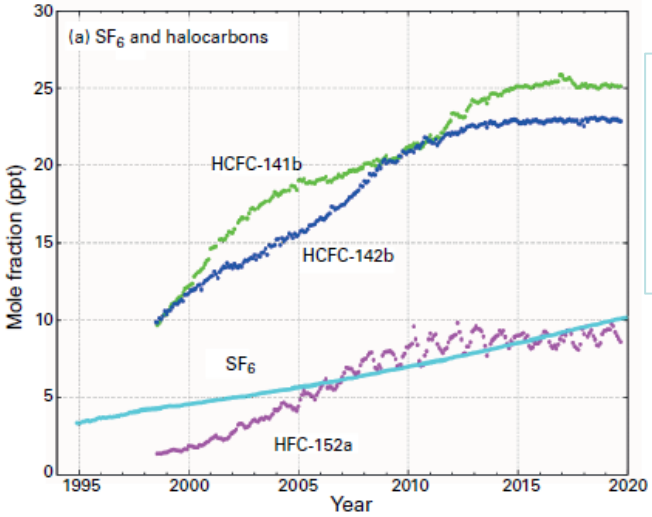
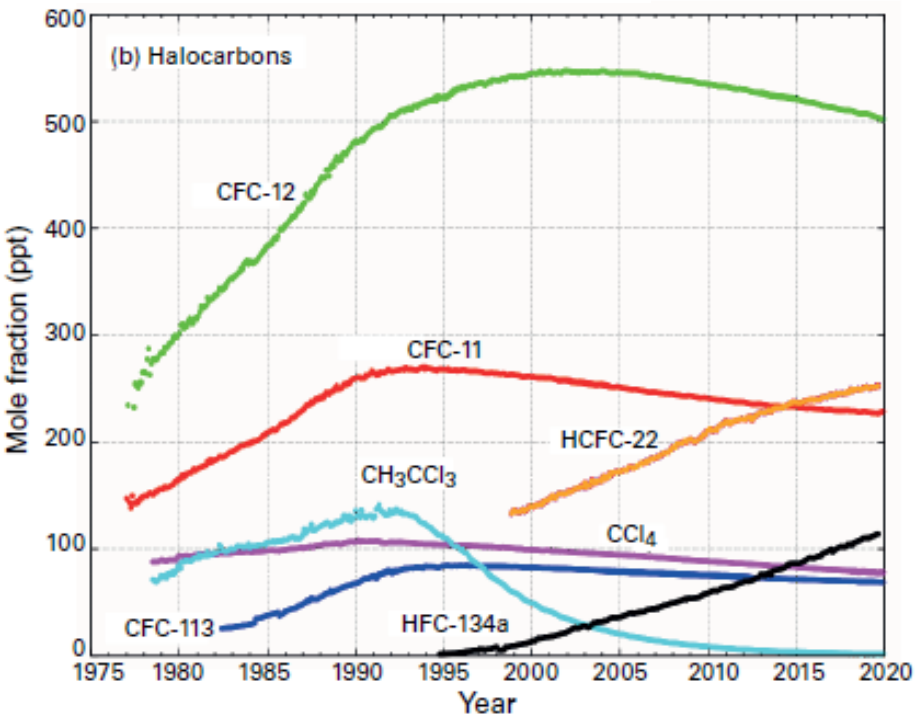
Trends and lifetimes of halogenated source gases





Lifetime in years	
CFC-12	102
CFC-11	52
CFC-113	93
HCFC-22	11.6
HFC-134a	13.5
CH_3CCl_3	5
CCl_4	30
CF_4	50000
SF_6	1065

Figure 9. Monthly mean mole fractions of sulfur hexafluoride (SF_6) and the most important halocarbons: (a) SF_6 and lower mole fractions of halocarbons and (b) higher halocarbon mole fractions. For each gas, the number of stations used for the analysis was as follows: SF_6 (87), CFC-11 (23), CFC-12 (25), CFC-113 (22), CCl_4 (21), CH_3CCl_3 (25), HCFC-141b (10), HCFC-142b (15), HCFC-22 (14), HFC-134a (11), HFC-152a (10)).

from WMO GHG Bulletin, n°18, 2022

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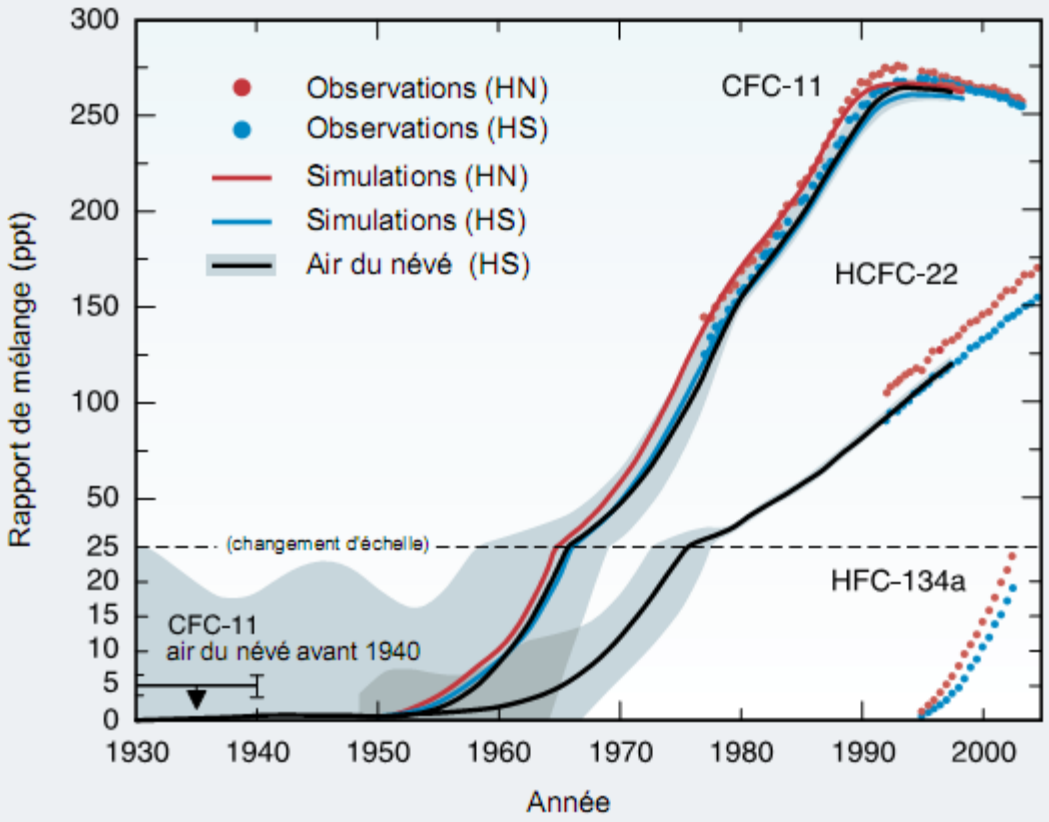
And before 1950 ?

Figure RT-3. Estimations des rapports de mélanges troposphériques mondiaux (ppt) de CFC-11, HCFC-22 et HFC-134a, présentés séparément pour les deux hémisphères Nord et Sud. Les symboles en rouge et bleu indiquent les mesures des réseaux AGAGE (*Advanced Global Atmospheric Gases Experiment*) et CMDL (*Climate Monitoring and Diagnostics Laboratory*), tandis que les lignes en rouge et bleu représentent les simulations des concentrations de CFC-11, extrapolées des estimations d'émission et de durée de vie dans l'atmosphère. Les lignes noires et les zones grisées représentent l'écart entre estimations et incertitudes pour le CFC-11 et le HCFC-22, dérivées de l'inversion de la synthèse des mesures de l'air du névé de l'Antarctique et des mesures atmosphériques *in situ* du Cap Grim. La grosse ligne noire horizontale avec la barre fléchée et la barre d'erreur indique une autre limite supérieure d'estimation des concentrations de CFC-11 avant 1940, fondée sur les mesures de l'air du névé au pôle Sud. À noter que les gaz présentés ici servent dans diverses applications et ne sont représentés qu'à titre d'illustration. [Figure 1.8]



Adequacy between emissions and atmospheric concentrations

Extrait du Résumé technique 'Préservation de la couche d'ozone et du système climatique planétaire' (http://www.ipcc.ch/pdf/special-reports/sroc/sroc_spmts_fr.pdf)

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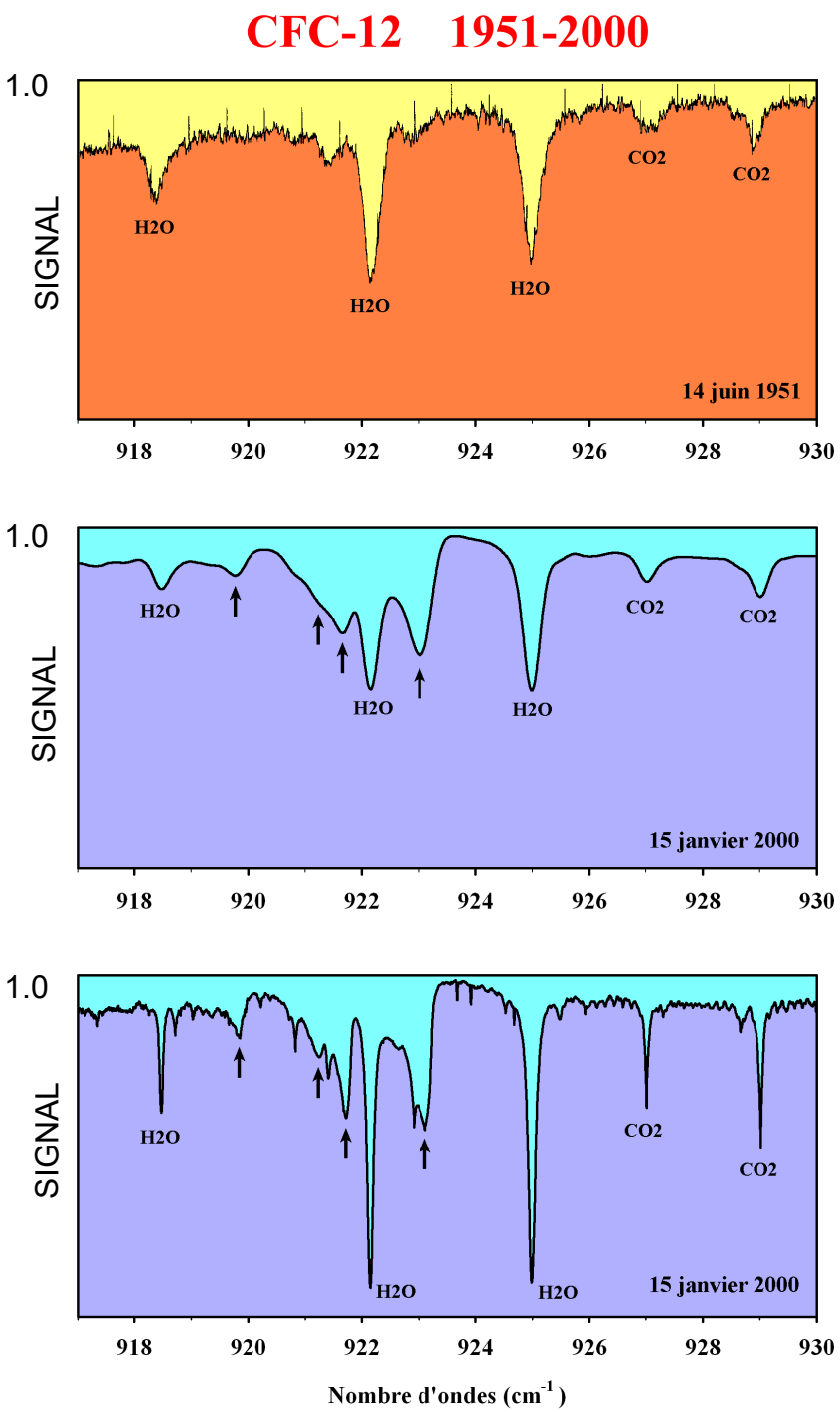
Comparison between IR observations obtained at the Jungfraujoch station:

- above, a recording from June 1951
- below, a recent observation obtained in 2000
- in the middle, the observation of 2000 degraded to the instrumental performances of the '50s
- arrows identify CFC-12 IR signatures
- these absorptions are absent from the 1951 spectrum



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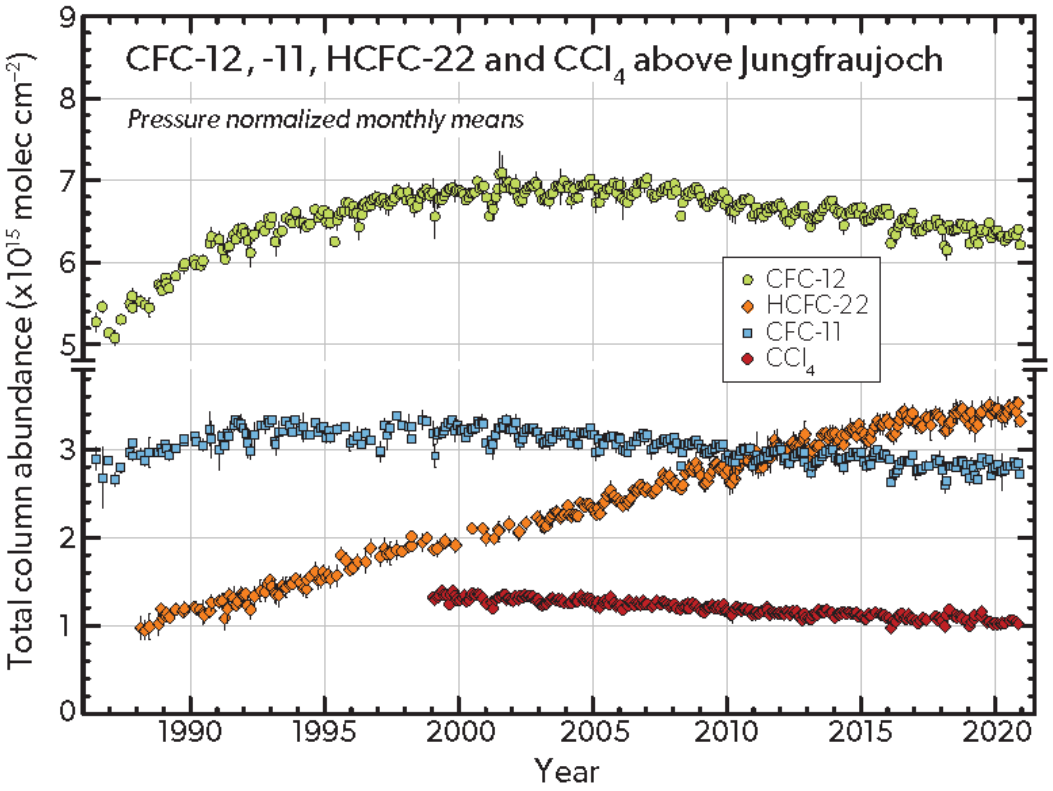

Figure 1-2. Monthly mean total vertical column abundance time series of CFC-12, CFC-11, HCFC-22, and CCl_4 derived from the long-term FTIR monitoring program conducted at the Jungfraujoch station, Switzerland (46.5°N), from 1986 to 2021 (updated from Zander et al., 2008; Gardiner et al., 2008; Rinsland et al., 2012; and Prignon et al., 2019). Note the discontinuity in the vertical scale.

Trends are still contrasted…

Substance	Annual trend 2014-2020 (%/yr rel. 2017)
CFC-12	-0.72 ± 0.09
HCFC-22	1.36 ± 0.13
CFC-11	-0.72 ± 0.19
CCl_4	-1.31 ± 0.22

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FTIR remote-sensing at Jungfraujoch

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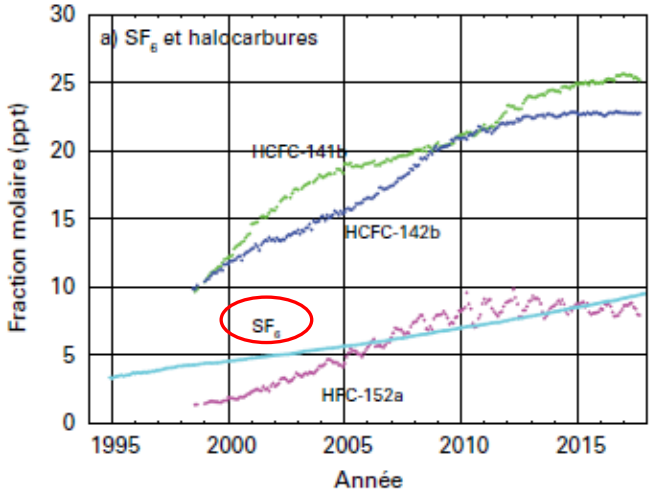
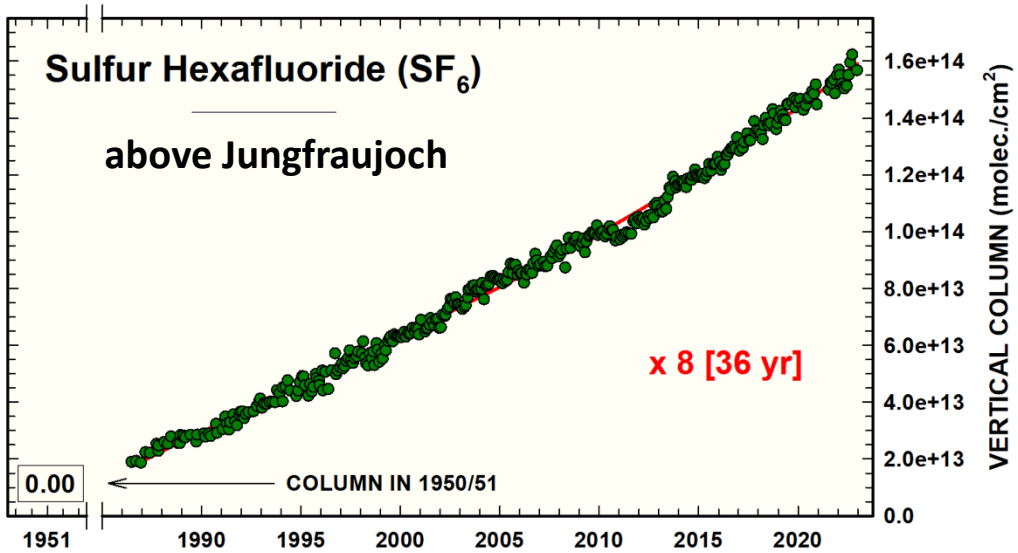


from WMO GHG Bulletin, n°14, November 2018

L'hexafluorure de soufre (SF_6) est un puissant gaz à effet de serre persistant. Produit par l'industrie chimique, il est utilisé surtout comme isolant dans les systèmes de distribution électrique. Sa fraction molaire représente plus du double aujourd'hui de ce qu'elle était au milieu des années 90 (figure 7 a)).

Figure 7. Évolution de la fraction molaire mensuelle moyenne du SF_6 et des principaux halocarbures: a) SF_6 et halocarbures aux faibles fractions molaires; b) halocarbures aux fractions molaires plus élevées. Nombre de stations utilisées pour les analyses: SF_6 (85), CFC-11 (23), CFC-12 (25), CFC-113 (21), CCl_4 (21), CH_3CCl_3 (24), HCFC-141b (9), HCFC-142b (14), HCFC-22 (13), HFC-134a (10), HFC-152a (9).



Substance	Annual trend 2014-2020 (%/yr rel. 2017)
SF_6	3.86 ± 0.14

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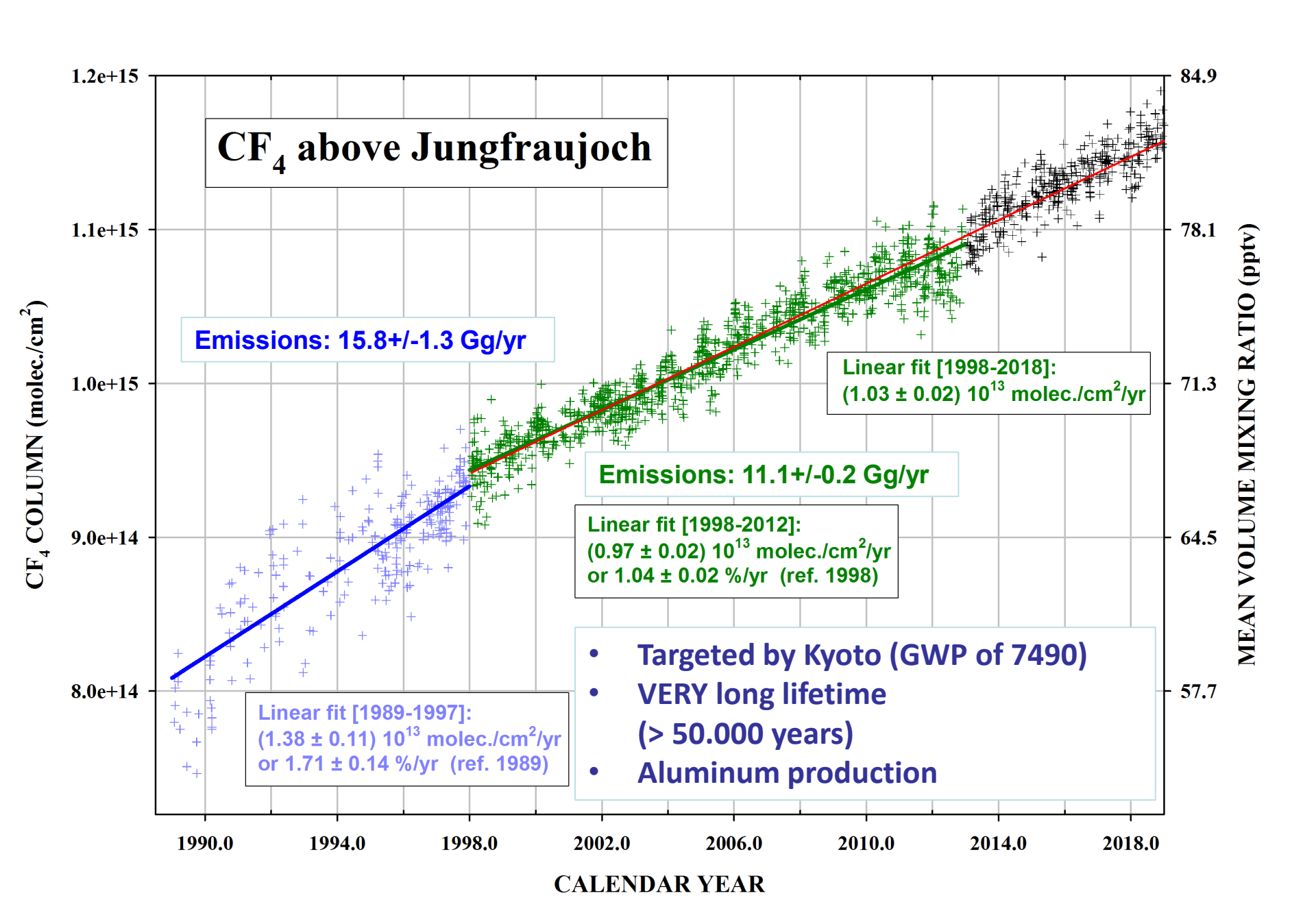
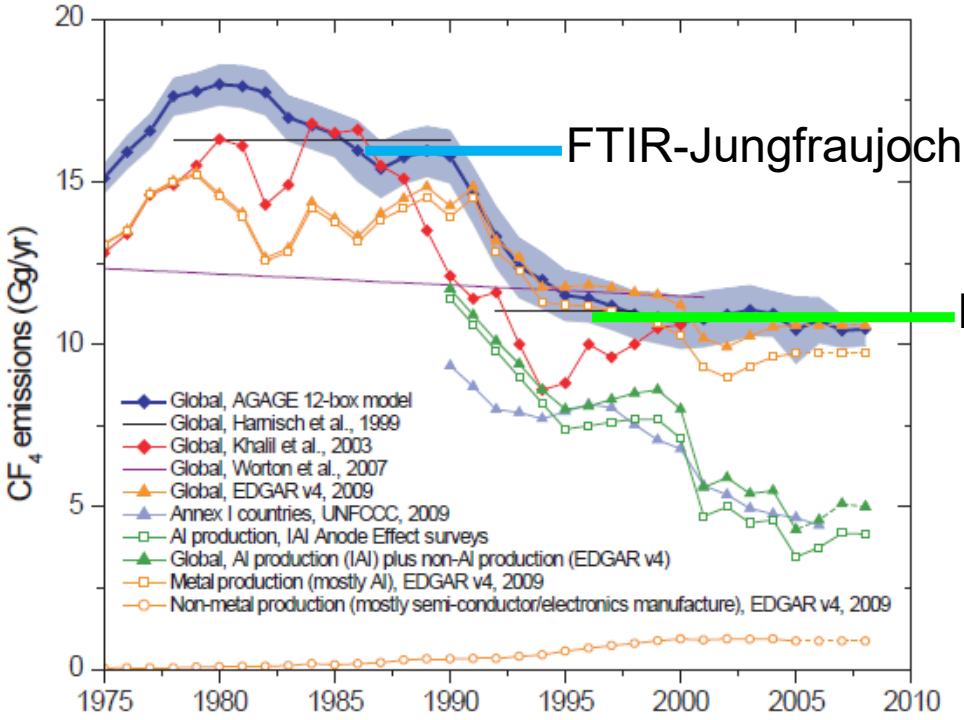


Gg or thousand of tons



FTIR-Jungfraujoch

FTIR-Jungfraujoch

Fig. 4. Global CF_4 emissions from the inversion of AGAGE atmospheric data with the AGAGE 2-D 12-box model compared to the emissions reported by Harnisch et al. (1999), Khalil et al. (2003), Worton et al. (2007), the EDGAR v4 (2009) emission database, and Annex I countries (UNFCCC, 2009, Table S1). Also shown are estimates of CF_4 emissions from Al production (IAI Anode Effect surveys), a global CF_4 emission estimate as the sum of these Al production CF_4 emissions and non-metal production related CF_4 emissions (EDGAR v4, mostly semiconductor/electronics manufacture), and the EDGAR v4 estimates for CF_4 emissions from metal production (mostly Al) and non-metal production. 2005 EDGAR v4 estimates have been used for 2005–2008 (shown as dashed line).

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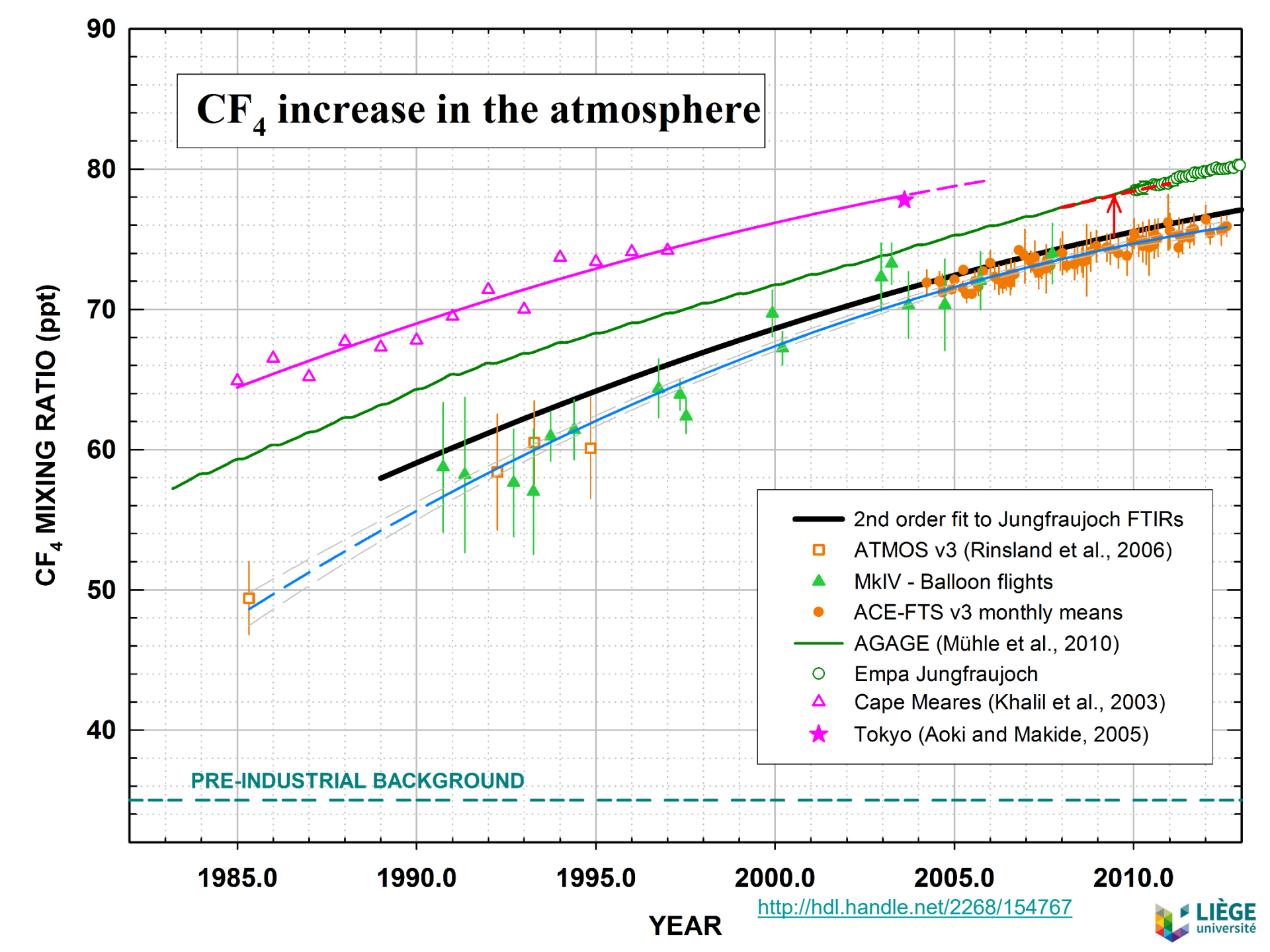
CF_4 increase in the atmosphere
CF_4 MIXING RATIO (ppt)
90
80
70
60
50
40
1985.0
1990.0
1995.0
2000.0
2005.0
2010.0
YEAR
2nd order fit to Jungfraujoch FTIRs
ATMOS v3 (Rinsland et al., 2006)
MkIV - Balloon flights
ACE-FTS v3 monthly means
AGAGE (Mühle et al., 2010)
Empa Jungfraujoch
Cape Meares (Khalil et al., 2003)
Tokyo (Aoki and Makide, 2005)
PRE-INDUSTRIAL BACKGROUND
http://hdl.handle.net/2268/154767
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Evolution of chlorine in the troposphere and stratosphere

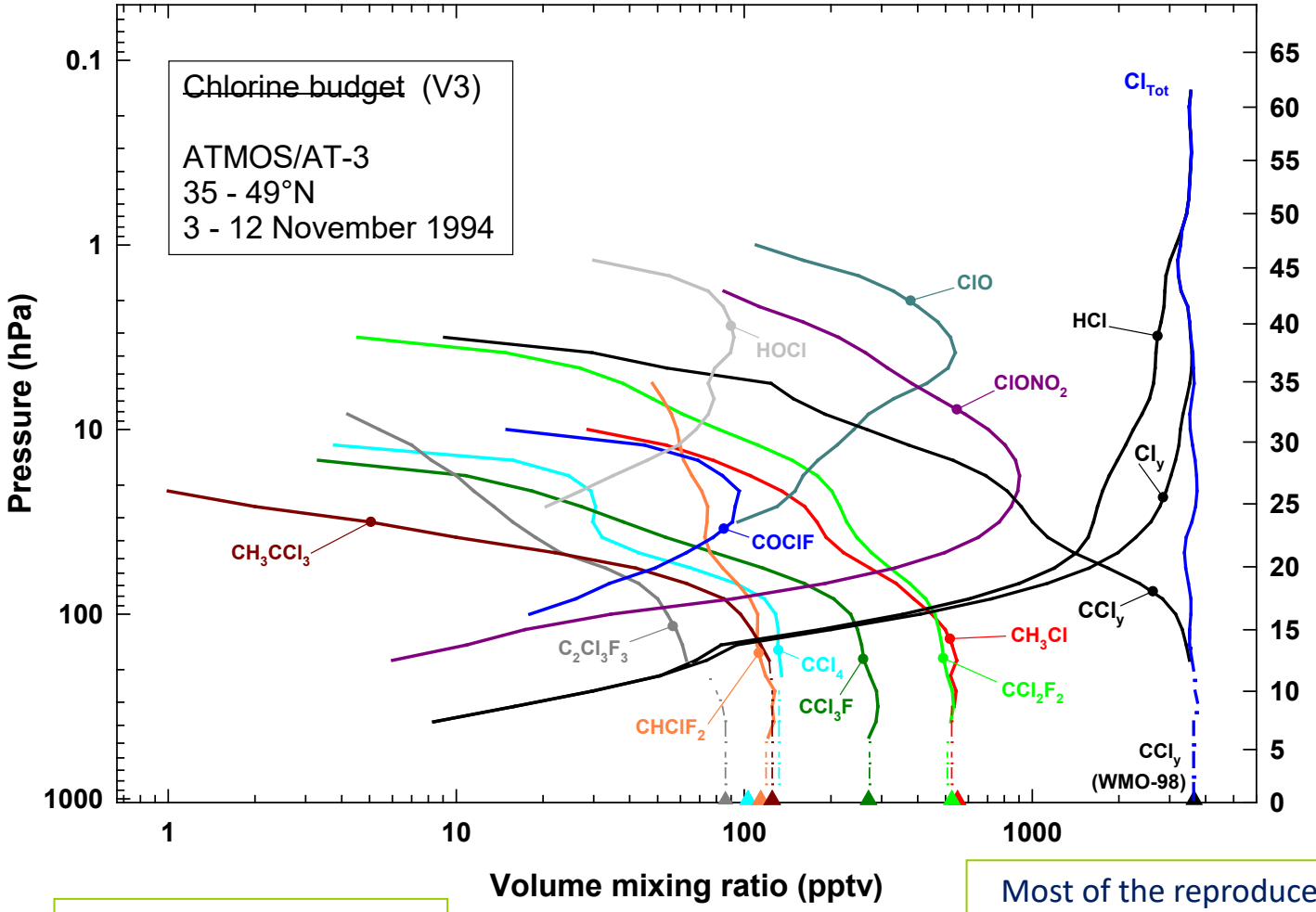
- In relation with the evolution of the concentrations of a series of GHGs affecting ozone
- The **organic chlorine budget (CCl_y)** is calculated by summing the concentrations of source/organic chlorine compounds emitted at the earth's surface, this summation is weighted by the number of Cl atoms contained in each of the compounds; this summation is written as follows :

  $$CCl_y = 2 \times [CCl_2F_2] + 3 \times [CCl_3F] + 3 \times [CCl_2FCClF_2] + [CHClF_2] + [CH_3Cl] + 3 \times [CH_3CCl_3] + 4 \times [CCl_4] + [secondary]$$

- A complex set of reactions will occur, mainly in the stratosphere, resulting in the redistribution of chlorine in the form of reactive species and stable reservoirs
- By including these species, the **budget of inorganic chlorine (Cl_y)** is established; similarly, it is written as follows :

  $$Cl_y = [HCl] + [ClONO_2] + [ClO] + [HOCl] + [COClF] + [secondary]$$

Distribution profiles of the main chlorinated constituents and partitioning



- We observe the conservation of chlorine in the atmosphere ⇒ no important species is missing in this budget
- At least 85% of the chlorine loading is anthropogenic
- The organic and inorganic chlorine profiles intersection is at about 20 km

$$Cl_{Tot} = CCl_y + Cl_y$$

Most of the reproduced profiles were measured by the ATMOS instrument, in **occultation**, from an American space shuttle

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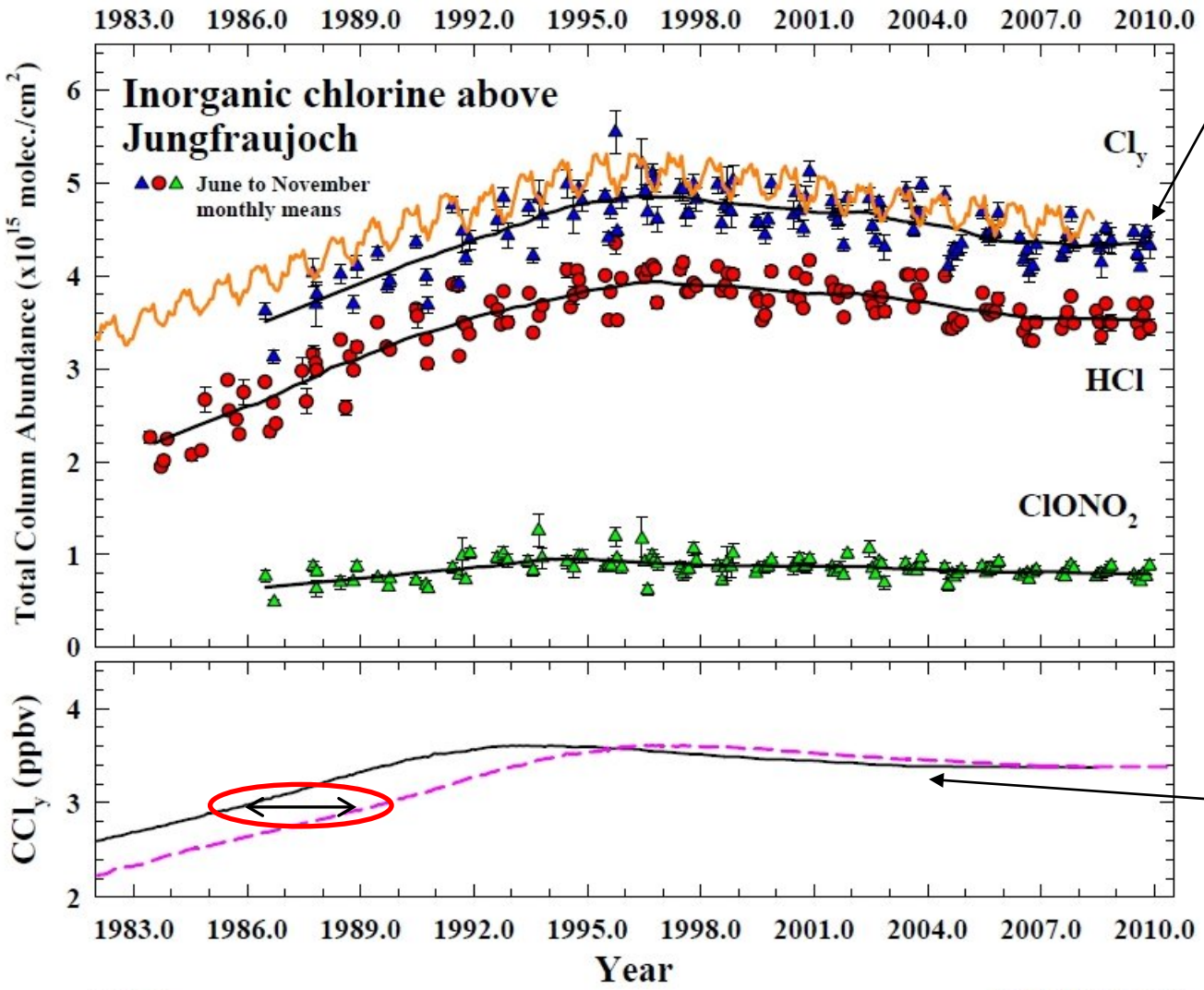
Evolution of chlorine in the troposphere and stratosphere



FTIR remote-sensing at Jungfraujoch (Cl_y)

- Growth ~4%/yr
- Decrease ~1%/yr
- Offset of maxima
- Models
- Success of Montreal Protocol => reduction of the chlorinated and brominated GHG threat on O_3 and the RF

in situ data (CCl_y)

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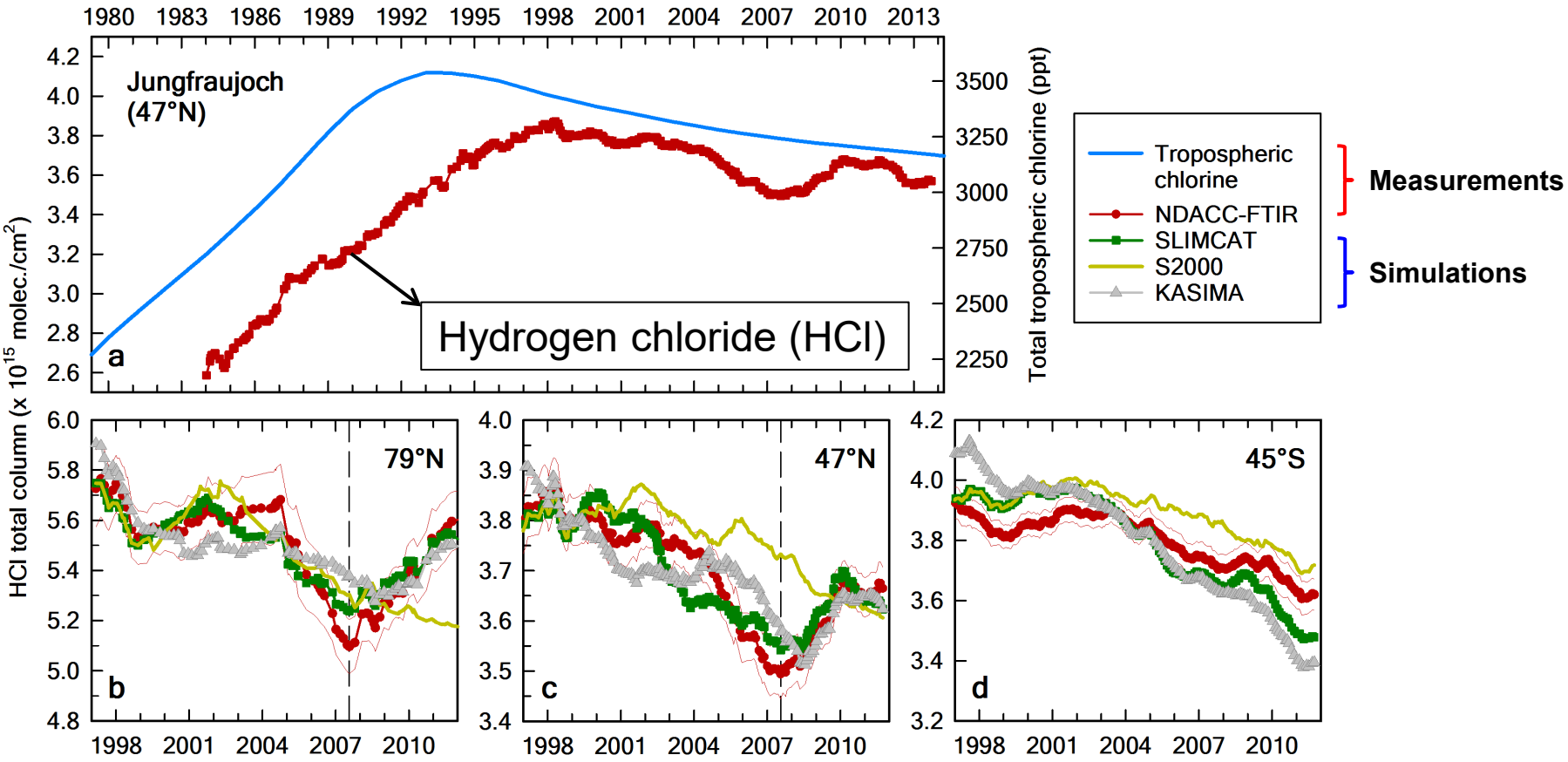
More recent evolution and atmospheric circulation



Multiyear anomaly explained by a slowing down of the atmospheric circulation of the Northern hemisphere lower stratosphere

Updated from Mahieu et al., 2014

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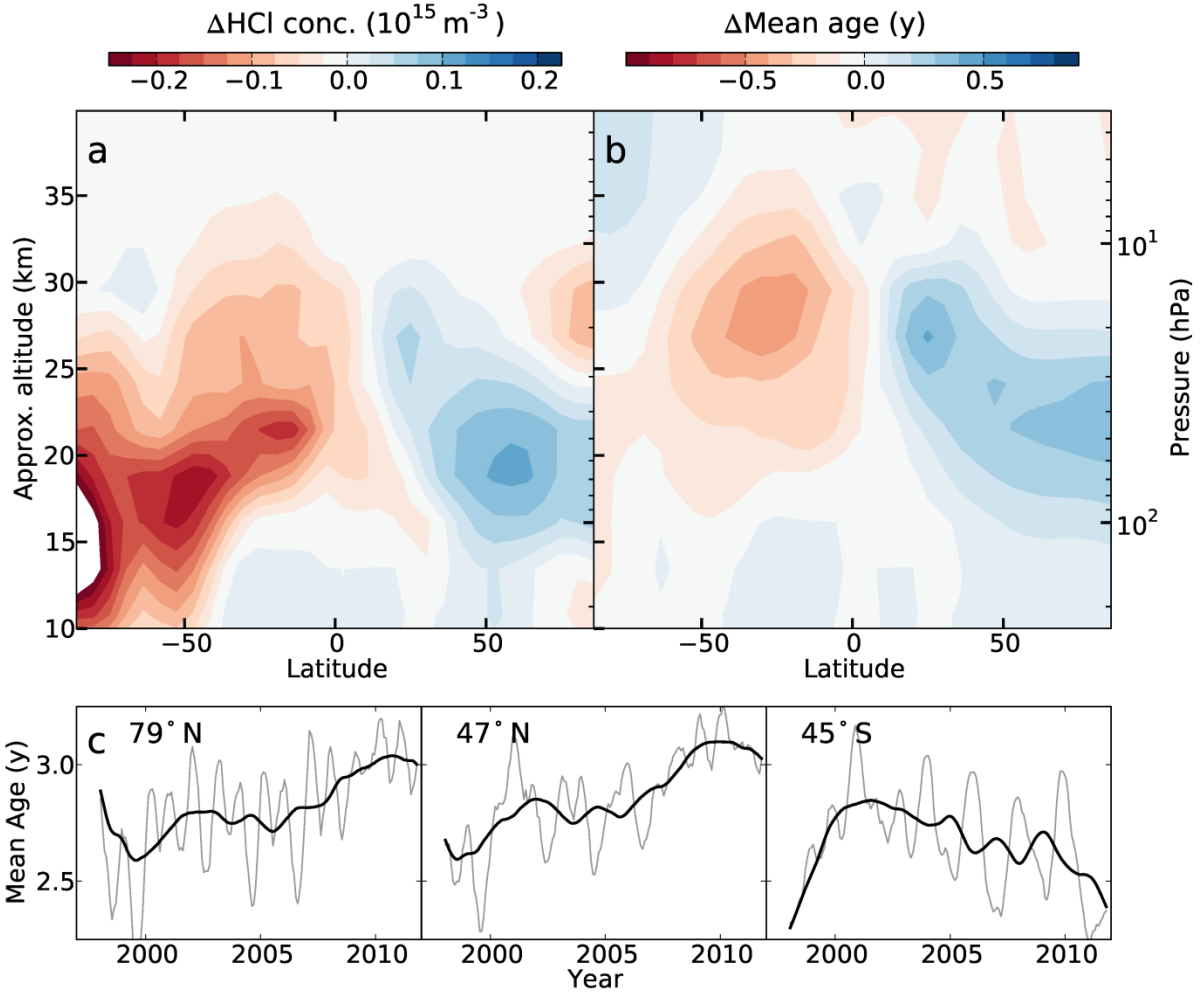
Spatial distribution of the HCl and age-of-air changes between 2005 and 2010



Derived from the SLIMCAT runs; Figure 4 in Mahieu et al., doi:10.1038/nature13857, 2014

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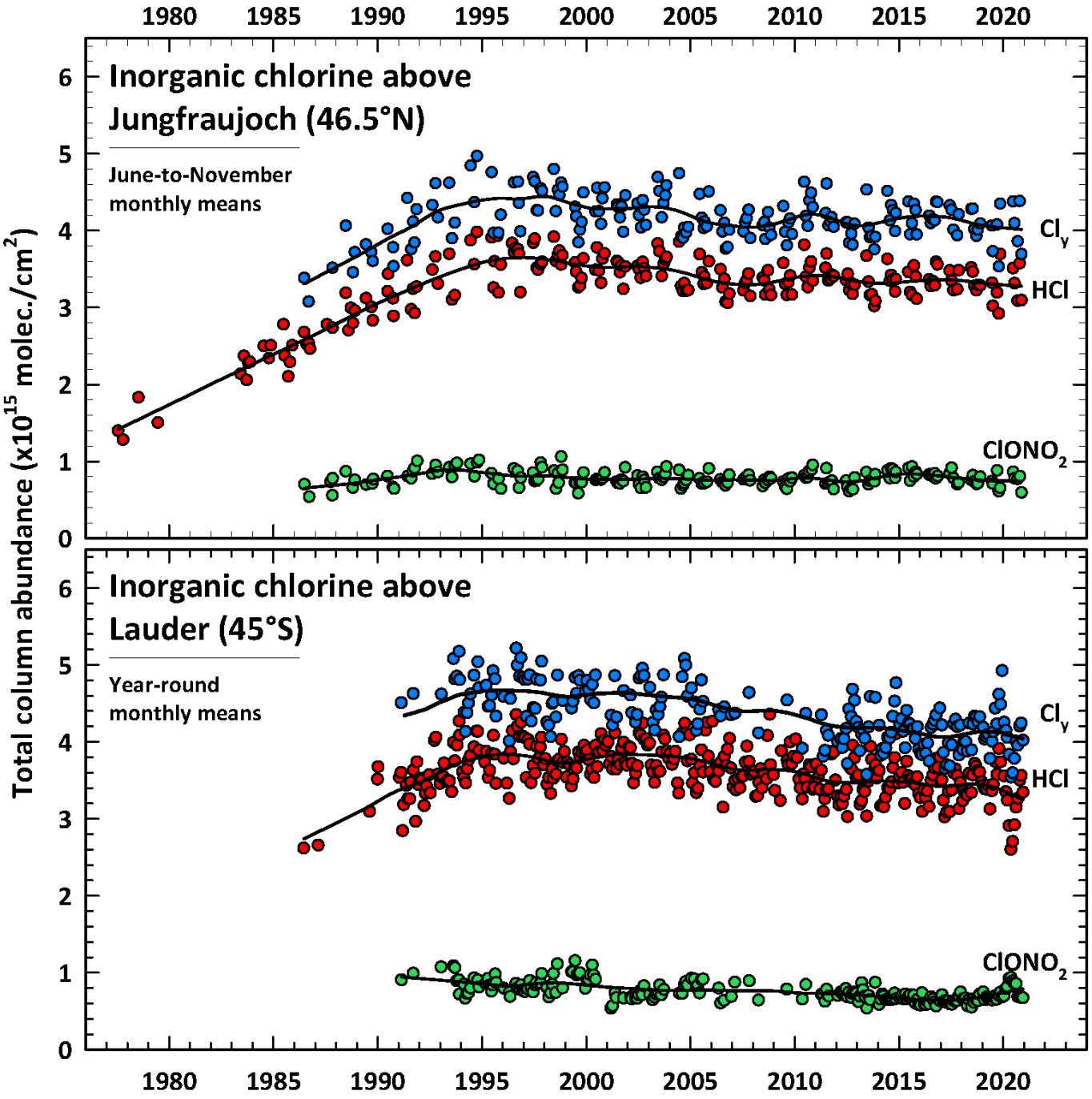

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