Greenhouse gas monitoring at the Zeppelin station
Annual report 2004

Report:	NILU OR 33/2005
TA reference no.:	TA-2110/2005
ISBN no.	82-425-1677-4
Employer:	Norwegian Pollution Control Authority (SFT)
Executing research institution:	Norwegian Institute for Air Research (NILU)
Authors:	O. Hermansen, N. Schmidbauer, C. Lunder, F. Stordal, A.M. Fjæraa, J. Schaug, C. Wehrli, I.T. Pedersen, K. Holmén, O.-A. Braathen (all NILU), J. Ström (Stockholm University)

Greenhouse gas monitoring at the Zeppelin station

Annual report 2004

Report
934
2005

Statlig program for forurensningsovervåking

Preface

In 1999 the Norwegian Pollution Control Authority (SFT) and NILU signed a contract commissioning NILU to run a programme for monitoring greenhouse gases at the Zeppelin station, close to Ny-Ålesund at Svalbard. At the same time NILU started to coordinate a project funded by the European Commission called SOGE (System for Observation of halogenated Greenhouse gases in Europe) The funding from SFT enabled NILU to broadly extend the measurement programme and associated activities, making the Zeppelin station a major contributor of data on a global as well as a regional scale.

The unique location together with the infrastructure of the scientific research community at Ny-Ålesund makes it a well suited platform for monitoring the global changes of ozone depleting substances (ODS) and greenhouse gases.

The measurement programme includes a range of chlorofluorocarbons (CFC), hydrofluorocarbons (HFC), hydrochlorofluorocarbons (HCFC), halones as well as other halogenated organic gases, sulphurhexafluoride (SF_6), methane (CH_4) and carbon monoxide (CO). The amount of particles in the air is measured by the use of an aethalometer and a Precision-Filter-Radiometer (PFR) sun photometer.

The station is also basis for measurements of carbon dioxide (CO_2) and particles performed by ITM, University of Stockholm. These activities are funded by the Swedish Environmental Protection Agency.

Data from the monitoring activities are processed and used as input data in the work on international agreements like the Kyoto and the Montreal Protocols.

This report summarises the activities and results of the climate monitoring programme during year 2004.

Contents

Summary

This annual report describes the activities and results in the project *Greenhouse gas monitoring at the Zeppelin station*, year 2004.

The report presents the Zeppelin monitoring station and some of the activities at the station, as well as current status for instruments and measurement methods used for the monitoring of climate gases. Results from the measurements are presented as monthly averages and plotted as daily averages. Annual averages and trends are also calculated. Since most of the ozone depleting substances are also strong climate gases, the monitoring gives important information concerning both climate change and depleting of the ozone layer

A wide range of anthropogenic as well as natural forcing mechanisms may lead to climate change. At present the known anthropogenic forcing mechanisms include well-mixed greenhouse gases (carbon dioxide, nitrous oxide, methane, SF_6 and halogenated hydrocarbons including CFCs, HFCs, HCFCs, halones and perfluorocarbons), ozone, aerosols (direct and indirect effects), water vapour and land surface albedo. A number of these gases have both a greenhouse effect and contribute to deplete the ozone layer.

In 1999 the Norwegian Pollution Control Authority (SFT) and NILU signed a contract commissioning NILU to run a programme for monitoring of climate gases at the Zeppelin station. The funding from SFT enables NILU to extend the greenhouse gas measurement programme and associated activities, making the Zeppelin station a major contributor of data on a global as well as a regional scale. The measurement programme at the Zeppelin station covers all major greenhouse gases - except N_2O (due to lack of instrumentation).

Measurements of greenhouse gases (including ozone depleting substances) at the Zeppelin station are used together with data from other remote stations for monitoring of global changes as well as for assessment of regional emissions and tracing of emission sources. Results from the greenhouse gas monitoring are used for assessment of compliance with the Montreal and Kyoto Protocols.

The **Montreal Protocol**, signed in 1987 and entered into force in 1989, is a very flexible instrument, which has been adjusted several times in the following years. It is still of vital interest that the scientific community is continuing and even expanding efforts in atmospheric measurements and modelling in order to follow the process over the next decades. Vital inputs in models like the lifetimes, atmospheric trends and emissions of compounds are still undergoing continuous review processes.

Climate Change and the **Kyoto Protocol** is a great environmental challenge to governments and the scientific community. Although there is superficial similarity between the topics of ozone depletion and those of climate change, and indeed much scientific interactions between the two, climate change has much wider implications. The range of materials and activities to be considered in regulations and the range of consequences are far larger and because of the long lifetime of carbon dioxide, the recovery from any effect on climate is far longer. There is a much larger gap to fill with both measurements and modelling.

For Kyoto Protocol substances only a very limited number of measurement sites exist that can deliver high quality and high time-frequent measurements. For Europe the number of sites, which can be used by modellers, is still far below 10. The measurements at Ny-Ålesund are an important contribution for European emission modelling.

Measurements so far confirm the Zeppelin station's status as a global background station for climate gas monitoring. As the data series are expanded over time, they will make a good basis for investigations of global levels and trends. Trend analysis of halogenated compounds based on four years data from Zeppelin are presented in this report.

The high frequency of data sampling enables studies of polluted air transport episodes. Combined with meteorological data and measurements from other European measurement stations, this is used for the investigation of regional emission inventories.

While the CFCs are about to level out or in case of CFC-11 decreasing, the HCFCs showing moderate increase rates, while the HFC concentrations in the atmosphere are still showing substantial increase.

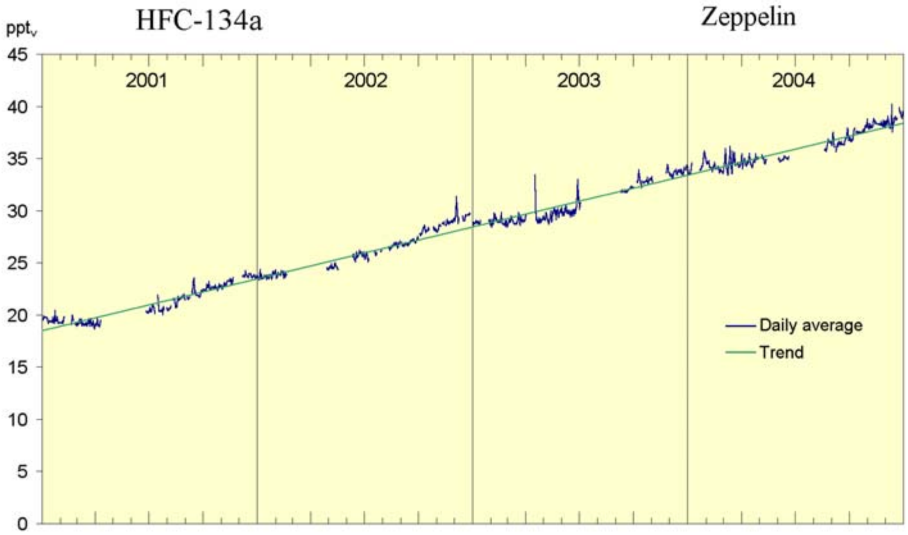


Figure A: Measurements of HFC-134a at the Zeppelin station indicates a doubling in consentration levels over the past four years.

To ensure the scientific level of greenhouse gas monitoring and related activities at the Zeppelin station, NILU is running the station on a budget in excess of available funding. Maintenance costs are continously increasing as monitoring instruments are getting older, resulting in gaps in data series and periods of data with reduced quality. At the same time new and improved instruments are being developed and implemented at other sites, enabling data of better precision, higher frequencies and including new compounds of interest .i.a. N_2O.

It will be a major challenge to retain the Zeppelin stations status as an internationally acknowledged global greenhouse gas monitoring site. This can only be maintained through the ongoing efforts of seeking new sources of funding for the scientific activities.

Table A: Monthly and yearly average concentration levels of greenhouse gases at the Zeppelin station year 2004. All concentrations in ppt_v, except for methane, carbon monoxide (ppb_v) and carbon dioxide (ppm_v).
Trends are calculated from data for the period 2001-2004.

Compound	**Formula**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Avg. 2004**	Trend pr. year
Methane	CH_4	1839		1843	1833		1803	1797	1792	1813	1812	1827	1836	1820	
Carbon monoxide	CO	145		178	165	138	107	96	99	107	111	125	143	128	
Carbondioxide*	CO_2	383	384	384	384	383	381	373	369	370	374	380	383	379	
Chlorofluorocarbons															
CFC-11	$CFCl_3$	263	259	260	259	259	257		262	259	259	260	261	260	- 1.1
CFC-12	CF_2Cl_2	567	565	558	558	564	560		560	560	562	562	564	562	+ 4.0
CFC-113	$CF_2ClCFCl_2$	84.2	84.0	82.8	82.5	81.9	81.6		82.1	81.2	81.2	81.4	81.5	82.2	+ 0.2
CFC-115	CF_3CF_2Cl	8.7	8.7	8.7	8.8	8.7	8.6		8.7	8.7	8.6	8.6	8.7	8.7	+ 0.1
Hydrofluorocarbons															
HFC-125	CHF_2CF_3	3.1	3.3	3.4	3.6	3.6	3.6		3.6	4.0	4.2	4.0	4.1	3.7	+ 0.6
HFC-134a	CH_2FCF_3	34.2	34.2	34.5	34.7	34.9	35.0		36.3	36.6	37.5	38.3	38.7	35.9	+ 5.0
HFC-152a	CH_3CHF_2	5.0	5.0	5.1	5.2	5.0	4.8		4.5	4.6	4.7	5.0	5.3	4.9	+ 0.7
Hydrochlorofluorocarbons															
HCFC-22	CHF_2Cl	181	181	181	182	182	181		183	183	183	185	186	183	+ 7.0
HCFC-141b	CH_3CFCl_2	19.9	19.7	19.7	19.8	19.8	19.7		19.6	19.6	19.6	19.7	19.9	19.7	+ 1.0
HCFC-142b	CH_3CF_2Cl	16.9	16.8	16.8	16.8	16.9	16.9		17.2	17.1	17.3	17.6	17.6	17.1	+ 0.7
Halons															
H-1301	CF_3Br	3.3	3.4	3.4	3.4	3.3	3.3		3.3	3.3	3.3	3.4	3.5	3.4	+ 0.1
H-1211	CF_2ClBr	4.7	4.7	4.7	4.7	4.7	4.7		4.7	4.6	4.6	4.7	4.7	4.7	+ 0.1
Halogenated compounds															
Methylchloride	CH_3Cl	576	587	591	590	587	554		495	484	503	526	548	549	+ 11.8
Methylbromide	CH_3Br	9.6	9.4	9.6	9.7	9.9	9.3		8.4	8.2	8.5	8.8	9.1	9.1	- 0.1
Methylendichloride	CH_2Cl_2	38.0	38.6	41.2	41.1	38.4	33.4		25.7	25.8	26.8	29.4	32.8	33.7	+ 0.6
Chloroform	$CHCl_3$	11.7	11.2	11.5	11.4	10.4	9.0		10.4	11.1	11.1	11.8	12.1	11.1	+ 0.03
Methylchloroform	CH_3CCl_3	24.4	24.0	24.0		23.3	22.5		21.0	20.5	20.2	20.1	19.8	22.0	- 4.7
TriChloroethylene	$CHClCCl_2$	1.5	1.0	1.8	0.7	0.3	0.2		0.2	0.4	0.3	0.2	1.7	0.7	+ 0.01
Perchloroethylene	CCl_2CCl_2	5.4	4.1	6.1	5.7	3.9	3.4		2.8	2.9	4.2	4.2	5.9	4.4	0.0
Sulphurhexafluoride	SF_6	5.4	5.5	5.5	5.6	5.6	5.7		5.8	5.8	5.7	5.7	5.8	5.7	

* Measurements of Carbondioxide performed by ITM, Stockholm University

1. Greenhouse gases and aerosols

1.1 Radiative forcing

Changes in climate are caused by internal variability within the climate system and external factors, natural and anthropogenic. The effect can be described through the effect on radiative forcing caused by each factor. Increasing concentrations of greenhouse gases tends to increase radiative forcing, hence contributing to a warmer global surface, while some types of aerosols have the opposite effect. Natural factors such as changes in solar output or explosive volcanic activities will also influence on radiative forcing. Changes in radiative forcing, relative to pre industrial time, are indicated in Figure 1.

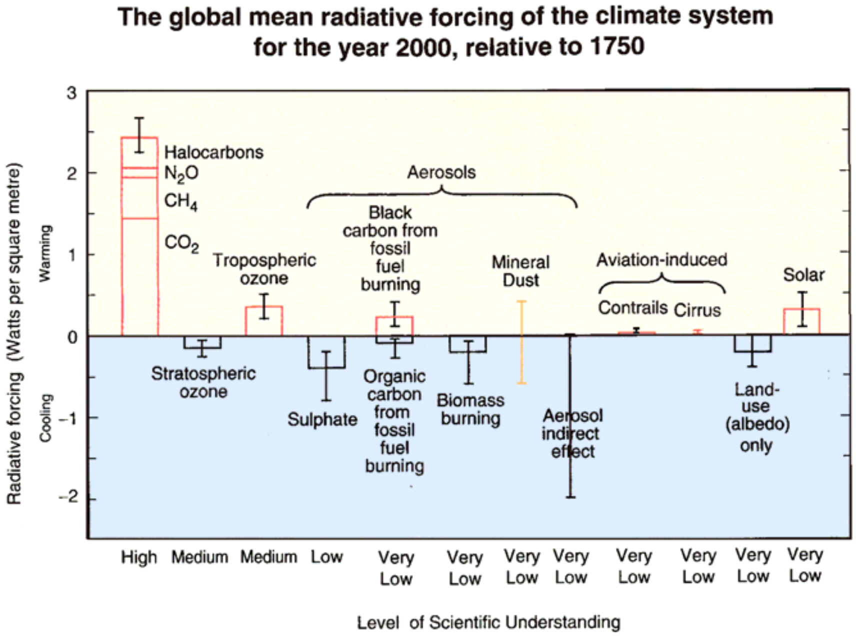


Figure 1: Known factors and their influence on radiative forcing relative to pre industrial time. The vertical lines indicate the uncertainties for each factor. (Source: IPCC.)

1.2 Natural greenhouse gases

Some gases in the atmosphere absorb the infrared radiation emitted by the Earth and emit infrared radiation upward and downward, hence raising the temperature near the Earth's surface. These gases are called greenhouse gases. Some of these gases have large natural sources, like carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). They have sustained a stable atmospheric abundance for the centuries prior to the industrial revolution. Emissions due to human activities have caused large increases in their concentration levels over the last century (figure 2), adding to radiative forcing.

The atmospheric concentration of CO_2 has increased by 30% since 1750. The rate of increase has been about 1.5 ppm (0.4%) per year over the last two decades. About three quarters of the anthropogenic emissions to the atmosphere is due to fossil fuel burning, the rest is mainly due to land-use change, especially deforestation.

The atmospheric concentration of CH_4 has increased by 1060 ppb (150%) since 1750 and continues to increase. More than half of the current emissions are anthropogenic; use of fossil fuel, cattle, rice plants and landfills. Carbon monoxide (CO) emissions have been identified as a cause of increasing CH_4 concentration. This is caused by CO reacting with reactive OH, thus preventing OH from reacting with CH_4, a primary loss reaction for methane (ref. Daniel, Solomon).

The atmospheric concentration of N_2O has increased by 45 ppb (17%) since 1750 and continues to increase. About a third of the emissions are anthropogenic; agriculture, cattle feed lots and chemical industry.

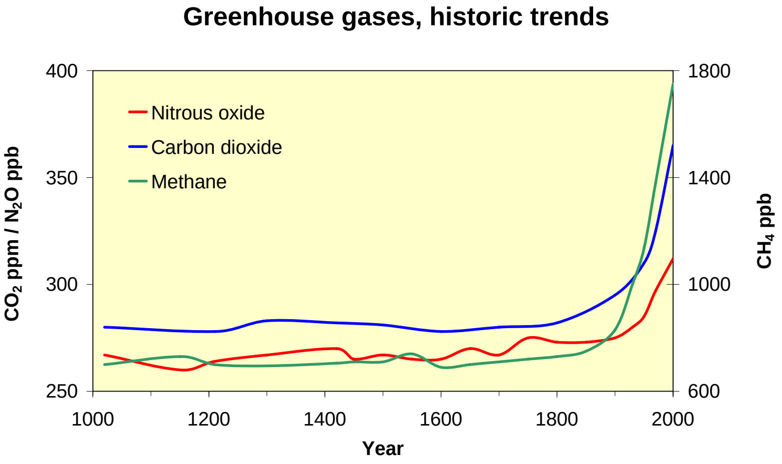


Figure 2: Changes in concentration levels over time for some natural greenhouse gases.

Ozone (O_3) is a reactive gas with relatively large variation in concentration levels. The amount of tropospheric O_3 has increased by 35% since 1750, mainly due to anthropogenic emissions of O_3-forming gases like volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides. O_3 forcing varies considerably by region and responds more quickly to changes in emissions than more long-lived greenhouse gases.

Water vapour in the lower stratosphere is an effective greenhouse gas. The amount of water vapour is temperature dependent, increasing with higher temperatures. Another source of H_2O is the oxidation of CH_4 and possibly future direct injection of H_2O from high-flying aircrafts.

1.3 Synthetic greenhouse gases

Another class of gases are the man made greenhouse gases, such as CFCs, HCFCs, HFCs PFCs, SF_6 and halons. These gases did not exist in the atmosphere before the 20th century. Although these gases have much lower concentration levels than the natural gases mentioned above, they are strong infrared absorbers, many of them with extremely long atmospheric lifetimes resulting in high global warming potentials (Table 1. Some of these gases are ozone depleting, and they are regulated by the Montreal protocol. Concentrations of these gases are increasing more slowly than before 1995, some of them are decreasing. Their substitutes, however, mainly HFCs, and other synthetic greenhouse gases are currently increasing.

Table 1: Halocarbons measured at Ny-Ålesund and their relevance to the Montreal and Kyoto Protocols.

Species	Chemical structure	Lifetime (years)	GWP[1]	Trend	**M**ontreal or **K**yoto Protocol	Comments on use
Chloro**f**luoro**c**arbons **(**CFCs**)**						
F-11	CCl_3F	45	4600	→↓	**M** phased out	foam blowing, aerosol propellent
F-12	CCl_2F_2	100	10600	→↓	**M** phased out	temperature control
F-113	CCl_2FCClF_2	85	6000	→↓	**M** phased out	solvent, electronics industry
F-114	$CClF_2CClF_2$	300	9800	→↓	**M** phased out	
F-115	CF_3CClF_2	1700	7200	→↓	**M** phased out	
Hydro**c**hloro**f**luoro**c**arbons (HCFCs**)**						
F-22	$CHClF_2$	12	1700	↑	**M** freeze	temperature control, foam blowing
F-124	CF_3CHClF	6	405	→	**M** freeze	temperature control
F-141b	CH_3CFCl_2	9	700	↑	**M** freeze	foam blowing, solvent
F-142b	CH_3CF_2Cl	19	2400	↑	**M** freeze	foam blowing
Hydro**f**luoro**c**arbons (HFCs**)**						
F-125	$C2HF_5$	29	3400	↑	**K**	temperature control
F-134a	CH_2FCF_3	14	1300	↑	**K**	temperature control, foam blowing, solvent , aerosol propellent
F-152a	$C_2H_4F_2$	1.4	120	↑	**K**	foam blowing
Halons						
F-1211	$CBrClF_2$	11	1300	→	**M** phased out	fire extinguishing
F-1301	$CBrF_3$	65	6900	→	**M** phased out	fire extinguishing
Per**f**luorinated **c**ompounds (PFCs)						
Sulfur hexafluoride	SF_6	3200	22200	→↑	**K**	Mg-production,electronics industry
Hexafluoro ethane	C_2F_6	10000	11900	→↑	**K**	Al-production,electronics industry
Other halogenated hydrocarbons						
Trichloroethane (Methyl chloroform)	CH_3CCl_3	5	140	↓↓	**M** phased out	solvent
Tetrachloro methane	CCl_4	35	1800	→↓	**M** phased out	solvent
Methyl chloride	CH_3Cl	1.5		(→↓)		natural emissions (algae)
Dichloro methane	CH_2Cl_2	0.5	9	→↓		solvent
Chloroform	$CHCl_3$	0.5	4	→↓		solvent
Trichloro ethylene	CCl_2CHCl			→↓		solvent
Perchloro ethylene	C_2Cl_4			→↓		solvent
Methyl bromide	CH_3Cl	1.2		→↓	**M** freeze: 1995	agriculture, natural emissions (algae)
Methyl iodide	CH_3I			→		natural emissions

[1]GWP(Global warming potensial) 100 years time periode, $CO_2 = 1$

1.4 Aerosols

Major sources of anthropogenic aerosols are fossil fuel and biomass burning. Aerosols like sulphate, biomass burning aerosols and fossil fuel organic carbon produce negative radiative forcing, while fossil fuel black carbon has a positive radiative effect. Aerosols vary considerably by region and respond quickly to changes in emissions.

Natural aerosols like sea salt, dust and sulphate and carbon aerosols from natural emissions are expected to increase as a result of climate change. In addition to their direct radiative forcing, aerosols have an indirect radiative forcing through their effect on cloud formation.

2. The Zeppelin station

2.1 Description of the station

The monitoring station is located on the Zeppelin Mountain, close to Ny-Ålesund at Svalbard. At 79° north the station is placed in an undisturbed arctic environment, away from major pollution sources. Situated 474 meters asl and most of the time above the inversion layer, there is minimal influence from local pollution sources in the nearby small community of Ny-Ålesund.

Figure 3: The monitoring station is located at the Zeppelin Mountain.

The Zeppelin station is owned and maintained by the Norwegian Polar Institute. NILU is responsible for the scientific activities at the station. The station was built in 1989-1990. After 10 years of use, the old building was no longer sufficient for operation of advanced equipment and the increasing amount of activities. The old building was removed to give place to a new modern station that was opened in May 2000. The new monitoring station was realised by funds from the Norwegian Ministry of Environment and the Wallenberg Institution via Stockholm University (SU).

The station building was constructed using selected materials to minimise contamination and influence on any ongoing measurements. All indoor air is ventilated away down from the mountain. The building contains several separate laboratories, some for permanent use by NILU and SU, others intended for short-term use like measurement campaigns and visiting scientists. A permanent data communication line permits on-line contact with the station for data reading and instrument control.

The unique location of the station makes it an ideal platform for the monitoring of global atmospheric change.

The measurement activities at the Zeppelin station contributes to a number of global, regional and national monitoring networks:

- SOGE (System for Observation of halogenated Greenhouse Gases in Europe)
- AGAGE (Advanced Global Atmospheric Gases Experiment)
- EMEP (European Monitoring and Evaluation Programme under "UN Economic Commission for Europe")
- Network for detection of stratospheric change (NDSC under UNEP and WMO)
- Global Atmospheric Watch (GAW under WMO)
- Arctic Monitoring and Assessment Programme (AMAP)

2.2 Activities at the station

2.2.1 NILU activities

The main goals of NILU's research activities at the Zeppelin station are:

- Studies of climate related matters and stratospheric ozone
- Exploration of atmospheric long range transport of pollutants
- Characterization of the arctic atmosphere and studies of atmospheric processes and changes

NILU performs measurements of halogenated greenhouse gases as well as methane and carbon monoxide using automated gas chromatographs with high sampling frequencies. A mass spectrometric detector is used to determine more than 30 halogenated compounds, automatically sampled 6 times per day. Methane and CO are sampled 3 times per hour. This high sampling frequency gives valuable data for the examination of episodes caused by long-range transport of pollutants as well as a good basis for the study of trends and global atmospheric change. Close cooperation with SOGE-partners on the halocarbon instrument and audits on the methane and CO-instruments (performed by EMPA on the behalf of GAW/WMO) show that the instruments deliver data of high quality.

The amount of particles in the air is monitored by a continuous aethalometer and by the use of a Precision-Filter-Radiometer (PFR) sun photometer. The aethalometer measures the total amount of particles at ground level, while the sun photometer measures the amount and size distribution through a total column.

The station at Zeppelin Mountain is also used for a long range of measurements, which are not directly related to climate gas monitoring, including daily measurements of sulphur and nitrogen compounds (SO_2, SO_4^{2-}, ($NO_3^- + HNO_3$) and ($NH_4^+ + NH_3$), main compounds in precipitation, mercury, persistent organic pollutants (HCB, HCH, PCB, DDT, PAH etc.), as well as tropospheric and stratospheric ozone.

2.2.2 ITM Stockholm University (SU)

At the Zeppelin station carbon dioxide (CO_2) and atmospheric particles are measured by Stockholm University (Institute of Applied Environmental Research, ITM).

SU maintains a continuous infrared CO_2 instrument, which has been monitoring since 1989. The continuous data are enhanced by the weekly flask sampling programme in co-operation with NOAA CMDL. Analysis of the flask samples provide CH_4, CO, H_2, N_2O and SF_6 data for the Zeppelin station.

The CO_2 monitoring project at the Zeppelin station has three goals:

- Provide a baseline measurement of European Arctic CO_2 concentrations.
- Allow detailed analysis of the processes behind CO_2 variations in the Arctic on time-scales from minutes to decades.
- Understand how human activities and climate change perturb the global carbon cycle and thus give variations of atmospheric CO_2 and CH_4.

SU has several instruments at Zeppelin station, which measure particles in the atmosphere. Aerosol particles tend to reflect light and can therefore alter the Earth's radiation balance. The Optical Particle Counter (OPC) gives the concentration of aerosol particles and, combined with data from the Nephelometer, clues to the particles' age and origin. Size distribution is acquired from a Differential Mobility Analyser (DMA).

Understanding atmospheric chemical processes requires more than just CO_2 and aerosols and scattering data. A total filter allows creating a bi-daily record of the chemical composition of aerosol particles.

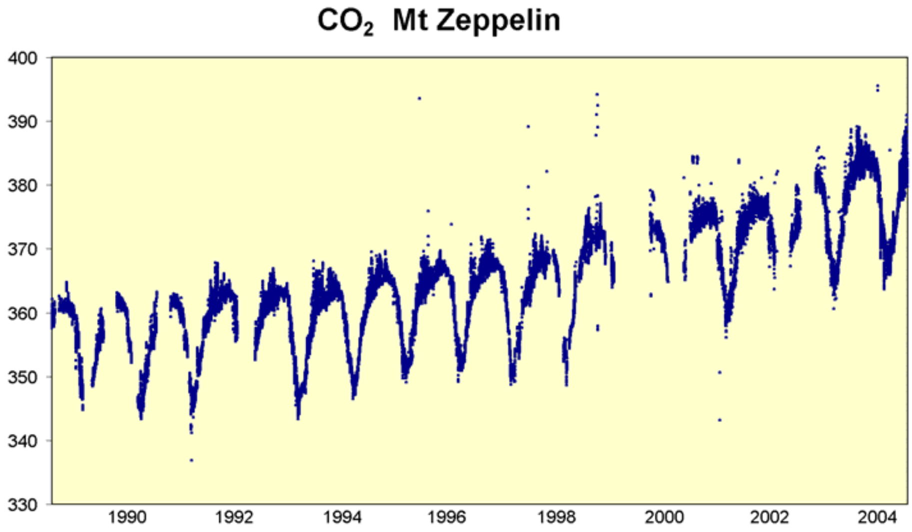


Figure 4: SU has been monitoring CO_2 at Mt. Zeppelin since 1989.

2.2.3 NOAA

NOAA CMDL (The Climate Monitoring and Diagnostics Laboratory at The National Oceanic and Atmospheric Administration in USA) operates a global air sampling network. The Zeppelin station is included in this network (Figure 5).

Air is sampled on a weekly basis in glass canisters and shipped to the laboratories at Boulder, Colorado (USA). The measurement programme includes CH_4, CO, H_2, N_2O and SF_6. Results from the analysis are used in studies of trends, seasonal variations and global distribution of greenhouse gases.

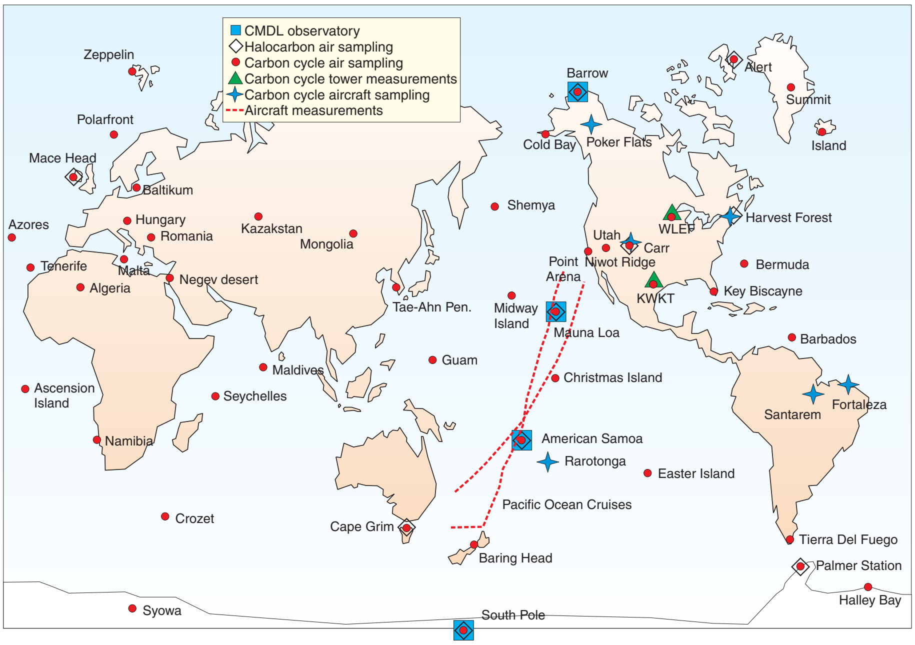


Figure 5: NOAA's global air sampling network.

2.3 SOGE

SOGE is an integrated system for observation of halogenated greenhouse gases in Europe. SOGE builds on a combination of observations and modelling. High resolution in situ observation at four background stations forms the backbone of SOGE. A network is being developed between the four stations. This includes full inter-calibration and common quality control, which is adopted from the global monitoring network of Advanced Global Atmospheric Gases Experiment (AGAGE).

The in situ measurements will be combined with vertical column measurements, which have been made at two of the network sites for up to about 15 years, as a part of Network for Detection of Stratospheric Change (NDSC). One purpose of this combination is determination of trends in the concentrations of the gases under consideration. Integration of the observations with a variety of model tools will allow extensive and original exploitation of the data. The integrated system will be used to verify emissions of the measured substances in Europe down to a regional scale. This will be obtained by the use of a model labelling air-parcels with their location and time of origin, so it is possible to identify the various sources that contribute to the concentrations measured at the network sites. The results will contribute to the assessment of compliance with the Kyoto and Montreal protocols, and they will be utilised also to define criteria for future monitoring of halocarbons in Europe.

Global models are used to estimate impacts of the observed compounds on climate change and the ozone layer. The impacts will be evaluated in terms of radiative forcing and Global Warming Potential (GWP), and ozone destruction and Ozone Depletion Potential (ODP), respectively.

SOGE is funded by European Commission Directorate General Research 5th Framework Programme Energy, Environment and Sustainable Development.

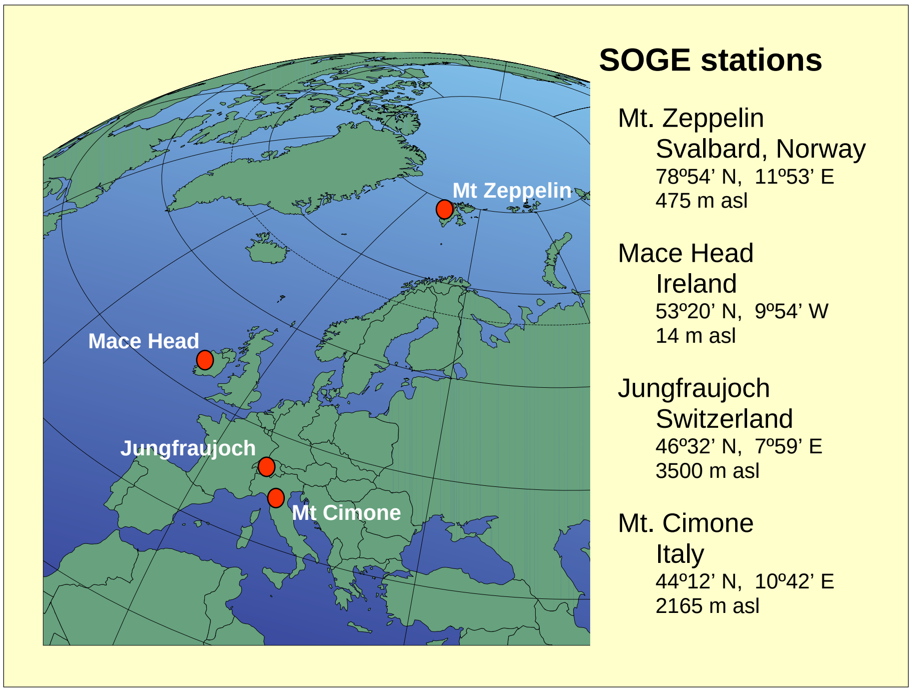


Figure 6: The SOGE climate gas monitoring stations.

2.4 AGAGE

The Advanced Global Atmospheric Gases Experiment and its predecessors the Atmospheric Lifetime Experiment (ALE) and the Global Atmospheric Gases Experiment (GAGE) have been measuring the composition of the global atmosphere since 1978. The observations and their interpretation are widely recognised for their importance to ozone depletion and climate change studies. The AGAGE is distinguished by its capability to measure over the globe at high frequency almost all of the important species in the Montreal Protocol to protect the ozone layer and almost all of the significant non-CO_2 gases in the Kyoto Protocol to mitigate climate change.

The scientific objectives of AGAGE are several in number and of considerable importance in furthering our understanding of a number of important global chemical and climatic phenomena:

- To optimally determine from observations, the rate of emission and/or chemical destruction (i.e. lifetime) of the anthropogenic chemicals which contribute most of the reactive chlorine and bromine released into the stratosphere.
- To accurately document the global distributions and temporal behaviour of the biogenic/anthropogenic gases N_2O, CH_4, CO, H_2, CH_3Cl, CH_3Br, $CHBr_3$, CH_3I, CH_2Cl_2, CCl_2CCl_2 and $CHCl_3$ over the globe.
- To optimally determine the average concentrations and trends of OH radicals in the troposphere by determining the rate of destruction of atmospheric CH_3CCl_3 and other hydrohalocarbons from continuous measurements of their concentrations together with industrial estimates of their emissions.

- To optimally determine, using CH_4 and N_2O data (and theoretical estimates of their rates of destruction), the global magnitude and distribution by semi-hemisphere or region of the surface sources of CH_4 and N_2O.
- To provide an accurate data base on the rates of accumulation of trace gases over the globe which cab be used to test the synoptic-, regional- and global-scale circulation predicted by three dimensional models and/or to determine characteristics of the sources of these gases near the stations.

The AGAGE measurement stations coastal sites around the world chosen to provide accurate measurements of trace gases whose lifetimes are long compared to global atmospheric circulations. The SOGE stations are included in the network through collaborations between SOGE and AGAGE sharing technology and placing AGAGE and SOGE data on common calibration scales with similar precision, accuracy and measurement frequency.

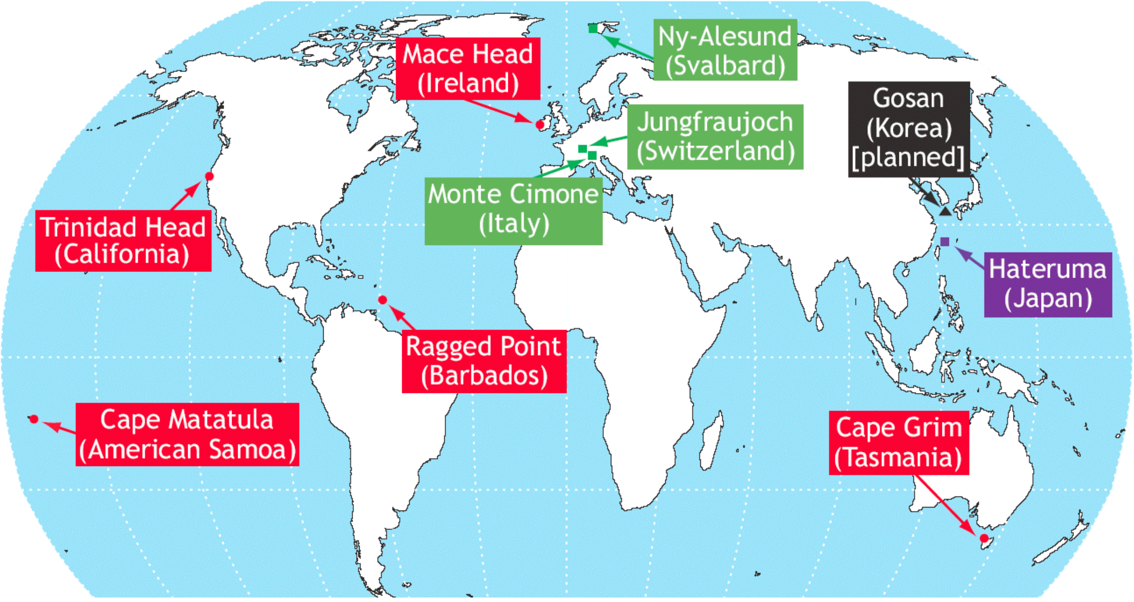


Figure 7: The AGAGE network of monitoring stations.

3. References

AMAP (1998) AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

Bousquet, P., Ciais, P., Peylin, P., Ramonet, M. and Monfray, P. (1999a) Inverse modeling of annual atmospheric CO_2 sources and sinks. 1. Method and control inversion. *J. Geophys. Res., 104*, 26,161-26,178.

Bousquet, P., Peylin, P., Ciais, P., Ramonet, M. and Monfray, P. (1999b) Inverse modeling of annual atmospheric CO_2 sources and sinks. 2. Sensitivity study. *J. Geophys. Res., 104,* 26,179-26,193.

Derwent, R.G., Ryall, D.B., Manning, A.J., Simmonds, P.G., O'Doherty, S., Biraud, S., Ciais, P., Ramonet, M. and Jennings, S.G. (2002) Continuous observations of carbon dioxide at Mace Head, Ireland from 1995 to 1999 and its net European ecosystem exchange. *Atmos. Environ., 36*, 2799-2807.

Derwent, R.G., Simmonds, P.G., O'Doherty, S., Ciais, P. and Ryall, D.B. (1998a) European source strengths and northern hemisphere baseline concentrations of radiatively active trace gases at Mace Head, Ireland. *Atmos. Environ., 32*, 3703-3715.

Derwent, R.G., Simmonds, P.G., O'Doherty, S. and Ryall, D.B. (1998b) The impact of the Montreal protocol on halocarbon concentrations in northern hemisphere baseline and European air masses at Mace Head, Ireland over a ten year period from 1987-1996. *Atmos. Environ., 32*, 3689-3702.

GAW homepage: http://gaw.kishou.go.jp/wdcgg.html

Grini, A., Myhre, G., Sundet, J.K. and Isaksen, I.S.A. (2002) Modeling the annual cycle of sea salt in the global 3D-model Oslo CTM-2, concentrations, fluxes and radiative impact. *J. Climate, 15*, 1717-1730.

Gurney, K.R. et al. (2002) Towards robust regional estimates of CO_2 sources and sinks using atmospheric transport models. *Nature, 415,* 626-629.

Heimann, M., and Kaminski, T. (1999) Inverse modelling approaches to infer surface trace gas fluxes from observed mixing ratios. In: *Approaches to scaling trace gas fluxes in ecosystems*. Ed. by A.F. Bowman. Amsterdam, Elsevier Science, pp. 277-295.

Houweling, S., Kaminski, T., Dentener, F., Lelieveld, J. and Heimann, M. (1999) Inverse modeling of methane sources and sinks using the adjoint of a global transport model. *J. Geophys. Res., 104*, 26,137-26,160.

Höhne, N. and Harnisch, J. (2002) Comparison of emission estimates derived from atmospheric measurements with national estimates of HFCs, PFCs and SF_6. In: *Proceedings of Third International Symposium on Non-CO_2 Greenhouse Gases (NCGG-3), Maastricht, the Netherlands, 21-23 January 2002*. Rotterdam, Millpress.

Høst, G. (1999) Bayesian estimation of European sulphur emissions using monitoring data and an acid deposition model. *Environ. Ecolog. Stat., 6*, 381-399.

Junge, C. (1963) Air chemistry and radioactivity. New York, Academic Press.

Kaminiski, T. and Heimann, M. (1999a) A coarse grid three-dimensional global inverse model of the atmospheric transport. 1. Adjoint model and Jacobian matrix. *J. Geophys. Res., 104*, 18,535-18,553.

Kaminiski, T. and Heimann, M. (1999b) A coarse grid three-dimensional global inverse model of the atmospheric transport. 2. Inversion of the transport of CO_2 in the 1980s. *J. Geophys. Res., 104*, 18,555-18,581.

Manning, A.J., Ryall, D.B., Derwent, R.G., Simmonds, P.G. and O´Doherty, S. (2003) Estimating European emissions of ozone-depleting and greenhouse gases using observations and a modeling back-attribution technique. *J. Geophys. Res., 108*, 4405, doi:10.1029/2002JD002312.

Ottar, B., Gotaas, Y., Hov, Ø., Iversen, T., Joranger, E., Oehme, M., Pacyna, J., Semb, A., Thomas, W. and Vitols, V. (1986) Air Pollutants in the Arctic. Final report of a research programme conducted on behalf of British Petroleum, LTD. Lillestrøm, Norwegian Institute for Air Research (NILU OR 30/86).

Reimann, S., Schaub, D., Weiss, A., Stemmler, K. and Hofer, P. (2002) Estimated emissions of halogenated greenhouse gases by analysis of on-line measurements at a high Alpine station (Jungfraujoch). In: *Proceedings of Third International Symposium on Non-CO_2 Greenhouse Gases (NCGG-3), Maastricht, the Netherlands, 21-23 January 2002*. Rotterdam, Millpress.

Reimann, S., Schaub, D., Stemmler, K., Folini, D., Hill, M., Hofer, P., Buchmann, B., Simmonds, P.G., Greally, B.R. and O´Doherty, S. (2004) Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, *J. Geophys. Res., 109*, D05307, doi:10.1029/2003JD003923.

Ryall, D.B., Derwent, R.G., Manning, A.J., Simmonds, P.G. and O'Doherty, S. (2001) Estimating source regions of European emissions of trace gases from observations at Mace Head. *Atmos. Environ., 35*, 2507-2523.

Schaug, J., Hansen, J.E., Nodop, K., Ottar, B. and Pacyna, J.M. (1987) Summary report from the the Chemical Co-ordination Centre for the third phase of EMEP. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Report 3/87).

Schaug, J. and Wehrli, C. (2004) Sun photometer measurements within WMO GAW in Ny-Ålesund at Spitzbergen, and in continental Europe during 2003. In: *Measurements of Particulate Matter: Status Report 2004.* Ed. by J. Schaug. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 3/2004).

Stordal F., Ellingsen K., Isaksen I.S.A., Manning A.J., Folini D. and Reimann S. (2004) Use of in situ observations and model calculations to constrain emissions of halogenated source gases. In: *Proceedings of the Quadrennial Ozon Symposium, Intern. Ozone Commission, Kos, Greece, June 2004.*

4. Acknowledgement

The AOD data from Gotland and Ispra have kindly been provided by Dr. Bertil Hakansson (SMHI) and Dr. Giuseppe Zibordi (JRC, Ispra).

To SOGE and Dr. Brian Greally, University of Bristol for providing data and trend results for the four SOGE stations.

To R.H.J. Wang (Georgia Tech., USA) and P.B. Krummel, CSIRO, Australia for kindly have been processed halocarbon data and trend analysis.

Appendix A

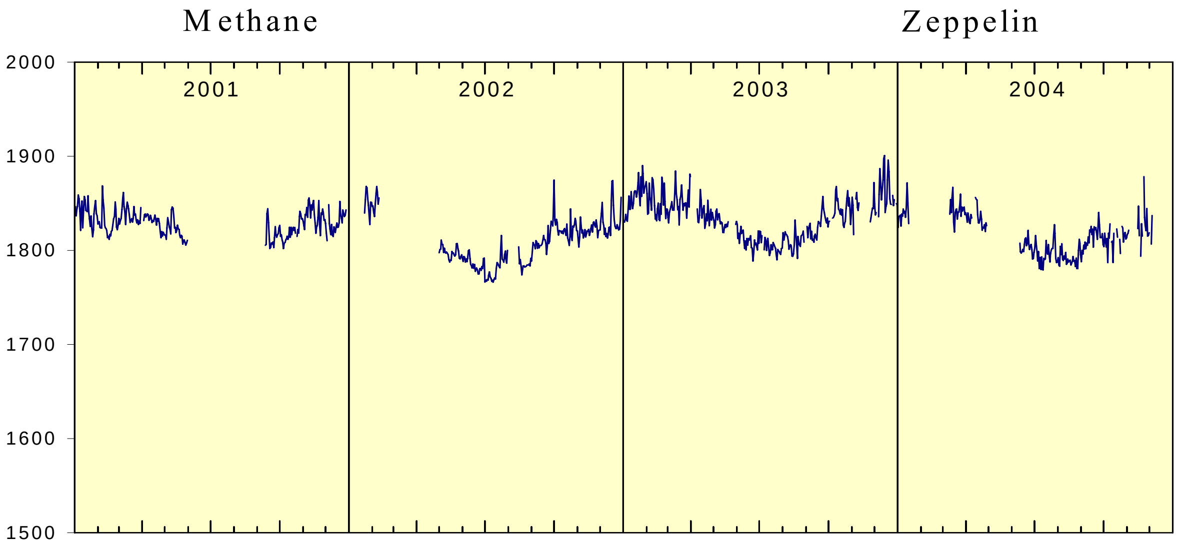
Measurement results

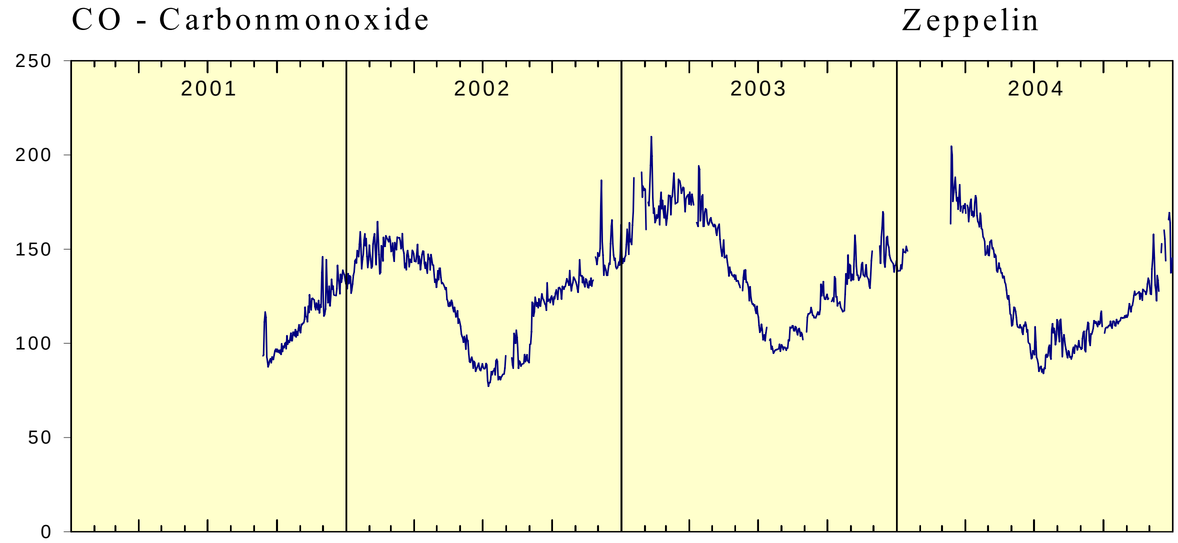
A.1 Greenhouse gases, levels and trends

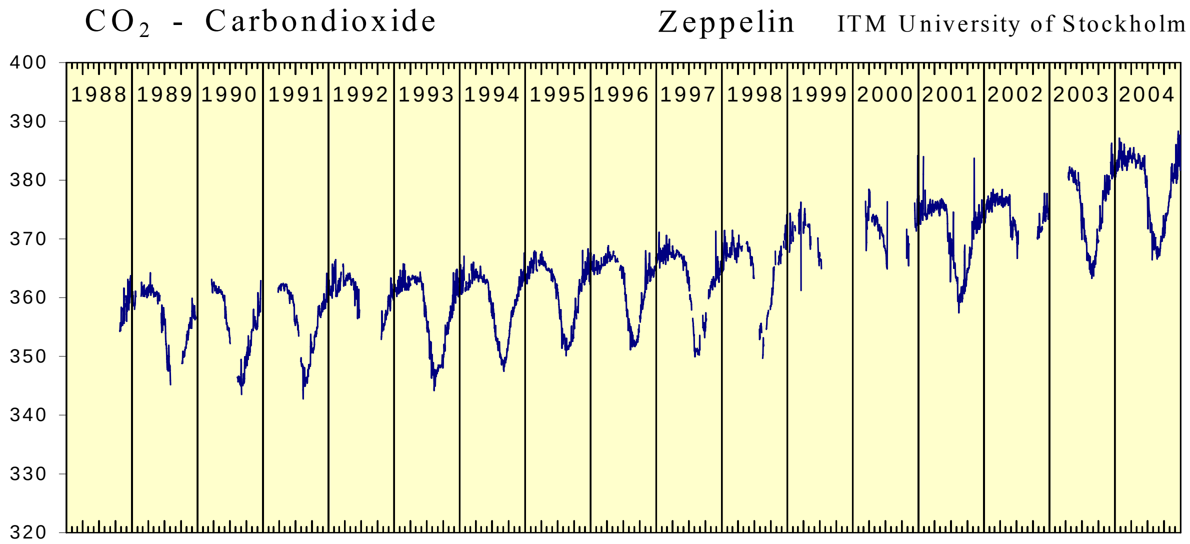
Table A.1: Monthly and yearly average concentration levels of greenhouse gases at the Zeppelin station year 2004. All concentrations in ppt_v*, except for methane and carbon monoxide (*ppb_v*). Trends are calculated from data for the period 2001-2004.*

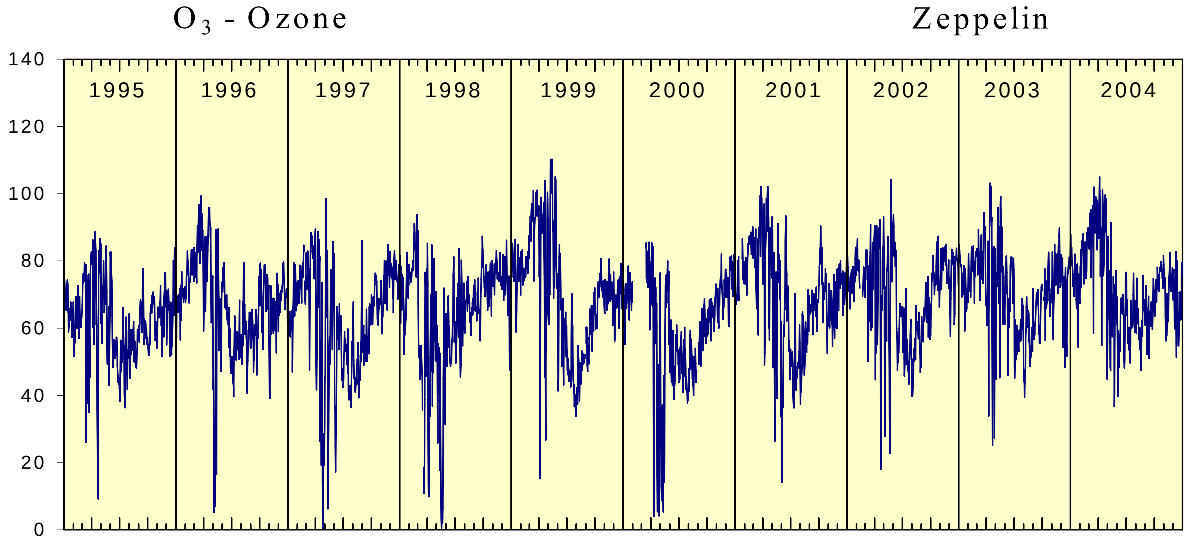
Compound	Formula	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Avg. 2004	Trend pr. year
Methane	CH_4	1839		1843	1833		1803	1797	1792	1813	1812	1827	1836	1820	
Carbon monoxide	CO	145		178	165	138	107	96	99	107	111	125	143	128	
Chlorofluorocarbons															
CFC-11	$CFCl_3$	263	259	260	259	259	257		262	259	259	260	261	260	- 1.1
CFC-12	CF_2Cl_2	567	565	558	558	564	560		560	560	562	562	564	562	+ 4.0
CFC-113	$CF_2ClCFCl_2$	84.2	84.0	82.8	82.5	81.9	81.6		82.1	81.2	81.2	81.4	81.5	82.2	+ 0.2
CFC-115	CF_3CF_2Cl	8.7	8.7	8.7	8.8	8.7	8.6		8.7	8.7	8.6	8.6	8.7	8.7	+ 0.1
Hydrofluorocarbons															
HFC-125	CHF_2CF_3	3.1	3.3	3.4	3.6	3.6	3.6		3.6	4.0	4.2	4.0	4.1	3.7	+ 0.6
HFC-134a	CH_2FCF_3	34.2	34.2	34.5	34.7	34.9	35.0		36.3	36.6	37.5	38.3	38.7	35.9	+ 5.0
HFC-152a	CH_3CHF_2	5.0	5.0	5.1	5.2	5.0	4.8		4.5	4.6	4.7	5.0	5.3	4.9	+ 0.7
Hydrochlorofluorocarbons															
HCFC-22	CHF_2Cl	181	181	181	182	182	181		183	183	183	185	186	183	+ 7.0
HCFC-141b	CH_3CFCl_2	19.9	19.7	19.7	19.8	19.8	19.7		19.6	19.6	19.6	19.7	19.9	19.7	+ 1.0
HCFC-142b	CH_3CF_2Cl	16.9	16.8	16.8	16.8	16.9	16.9		17.2	17.1	17.3	17.6	17.6	17.1	+ 0.7
Halons															
H-1301	CF_3Br	3.3	3.4	3.4	3.4	3.3	3.3		3.3	3.3	3.3	3.4	3.5	3.4	+ 0.1
H-1211	CF_2ClBr	4.7	4.7	4.7	4.7	4.7	4.7		4.7	4.6	4.6	4.7	4.7	4.7	+ 0.1
Halogenated compounds															
Methylchloride	CH_3Cl	576	587	591	590	587	554		495	484	503	526	548	549	+ 11.8
Methylbromide	CH_3Br	9.6	9.4	9.6	9.7	9.9	9.3		8.4	8.2	8.5	8.8	9.1	9.1	- 0.1
Methylendichloride	CH_2Cl_2	38.0	38.6	41.2	41.1	38.4	33.4		25.7	25.8	26.8	29.4	32.8	33.7	+ 0.6
Chloroform	$CHCl_3$	11.7	11.2	11.5	11.4	10.4	9.0		10.4	11.1	11.1	11.8	12.1	11.1	+ 0.03
Methylchloroform	CH_3CCl_3	24.4	24.0	24.0		23.3	22.5		21.0	20.5	20.2	20.1	19.8	22.0	- 4.7
TriChloroethylene	$CHClCCl_2$	1.5	1.0	1.8	0.7	0.3	0.2		0.2	0.4	0.3	0.2	1.7	0.7	+ 0.01
Perchloroethylene	CCl_2CCl_2	5.4	4.1	6.1	5.7	3.9	3.4		2.8	2.9	4.2	4.2	5.9	4.4	0.0
Sulphurhexafluoride	SF_6	5.4	5.5	5.5	5.6	5.6	5.7		5.8	5.8	5.7	5.7	5.8	5.7	

A.2 Non-halogenated greenhouse gases

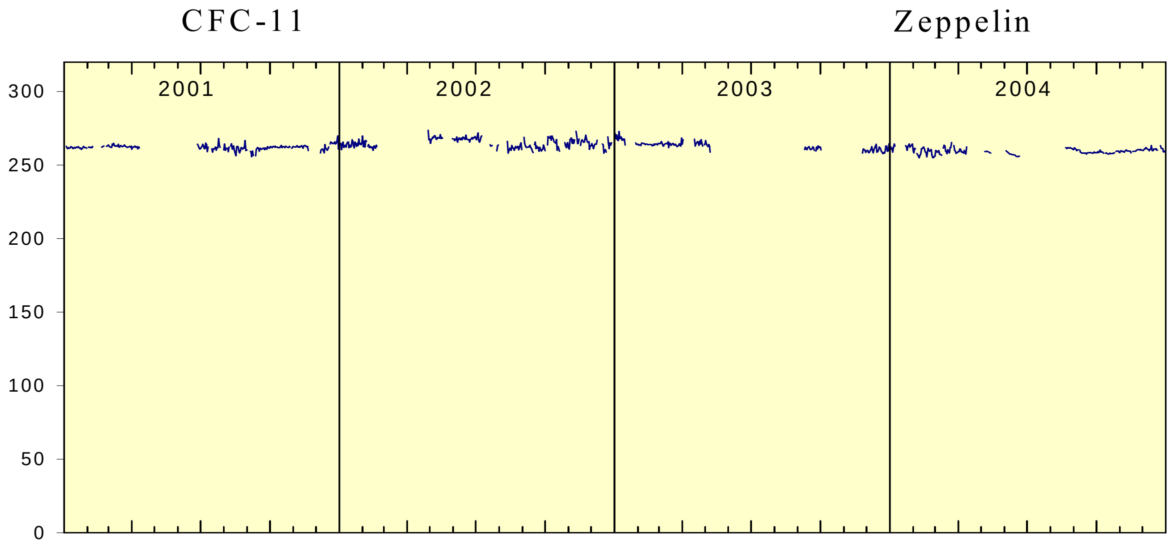


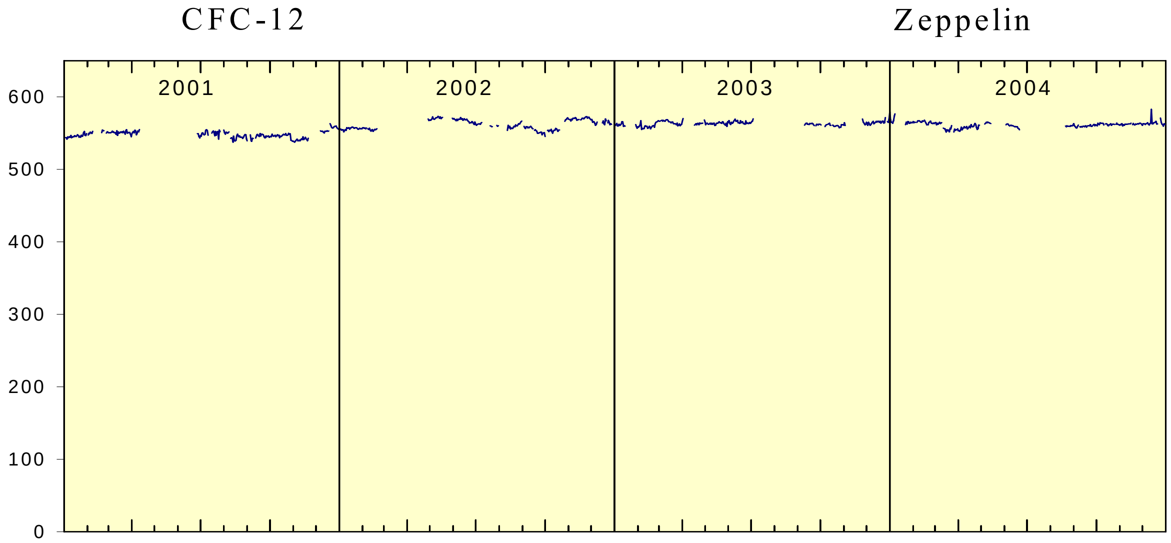


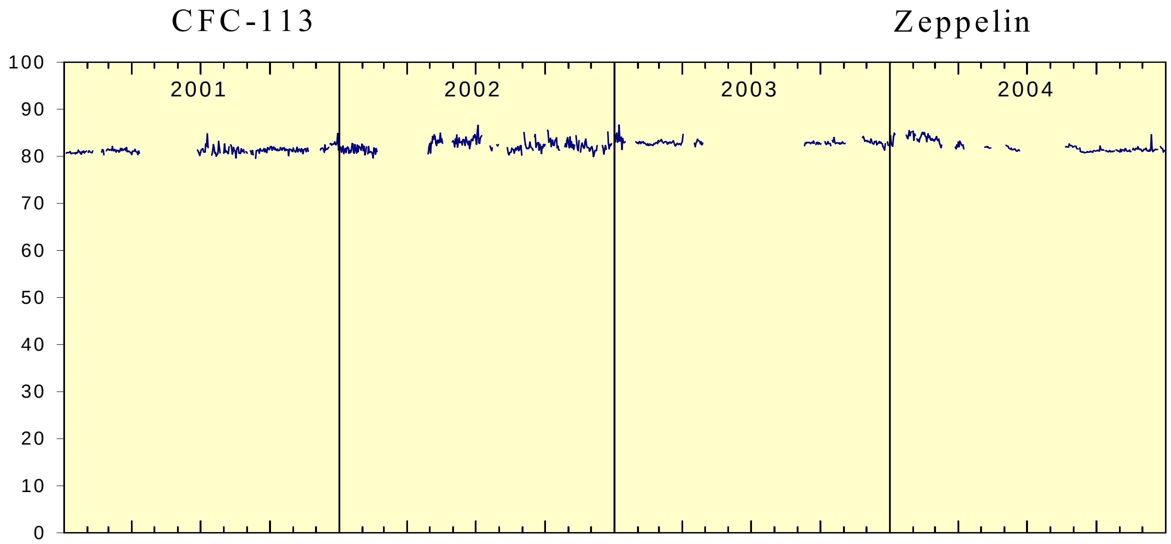


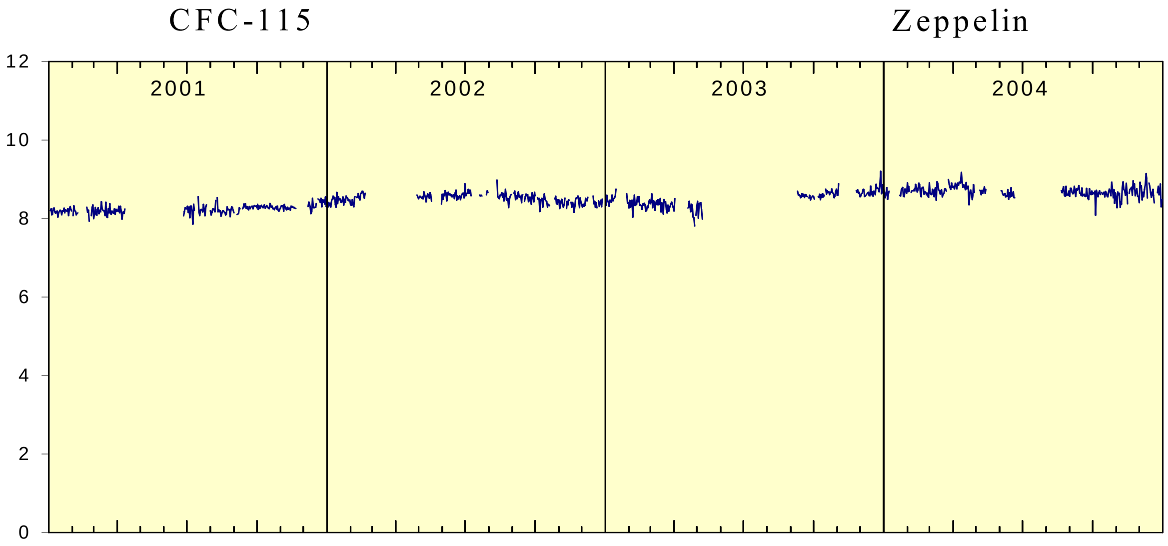

O_3 - Ozone
Zeppelin
140
120
100
80
60
40
20
0
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004

A.3 Chlorofluorocarbons (CFC)

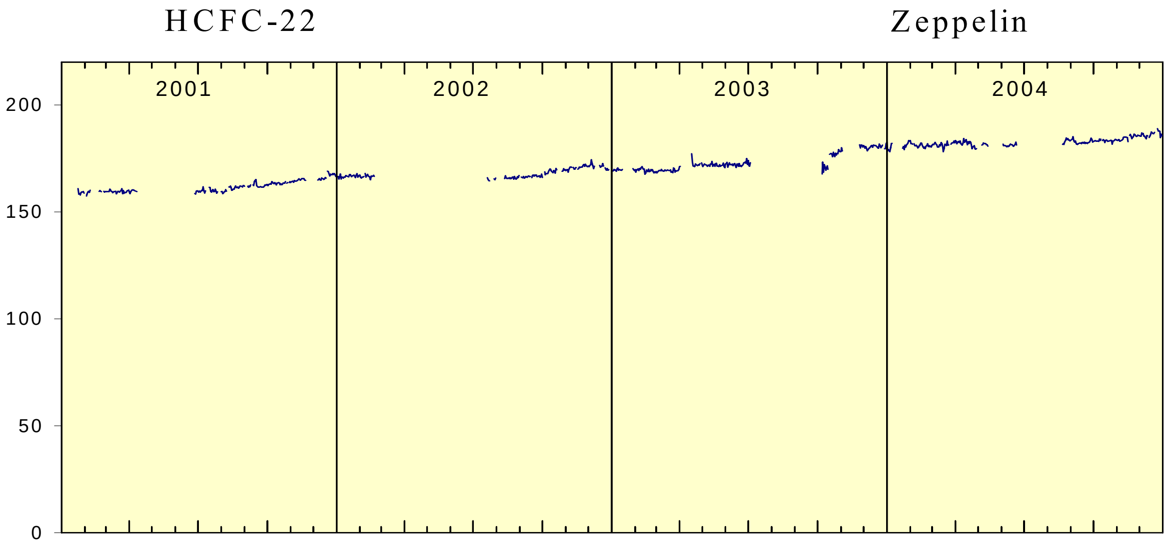


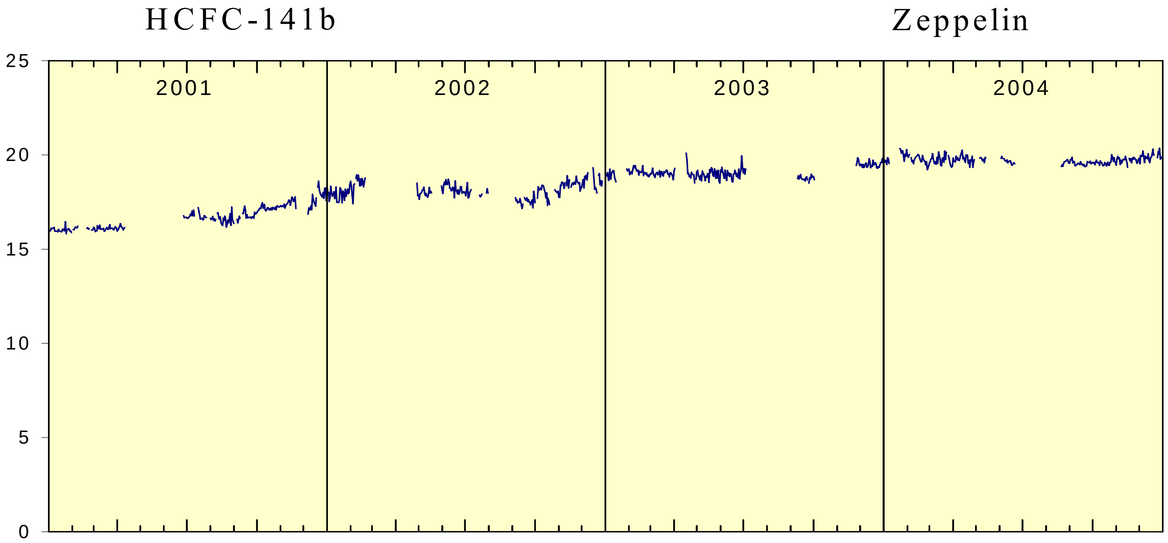


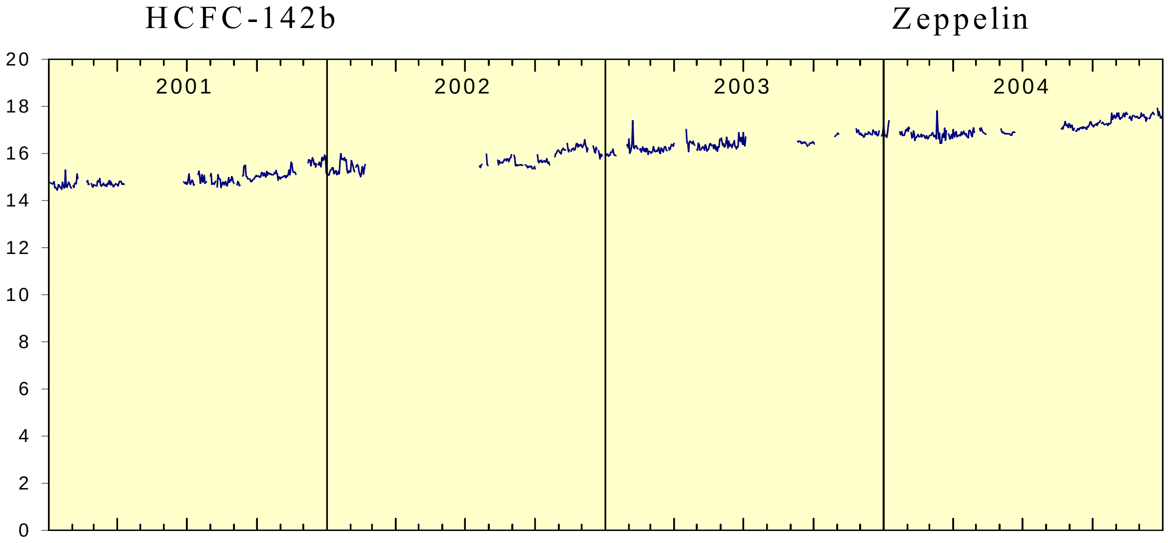



CFC-115
Zeppelin
12
10
8
6
4
2
0
2001
2002
2003
2004

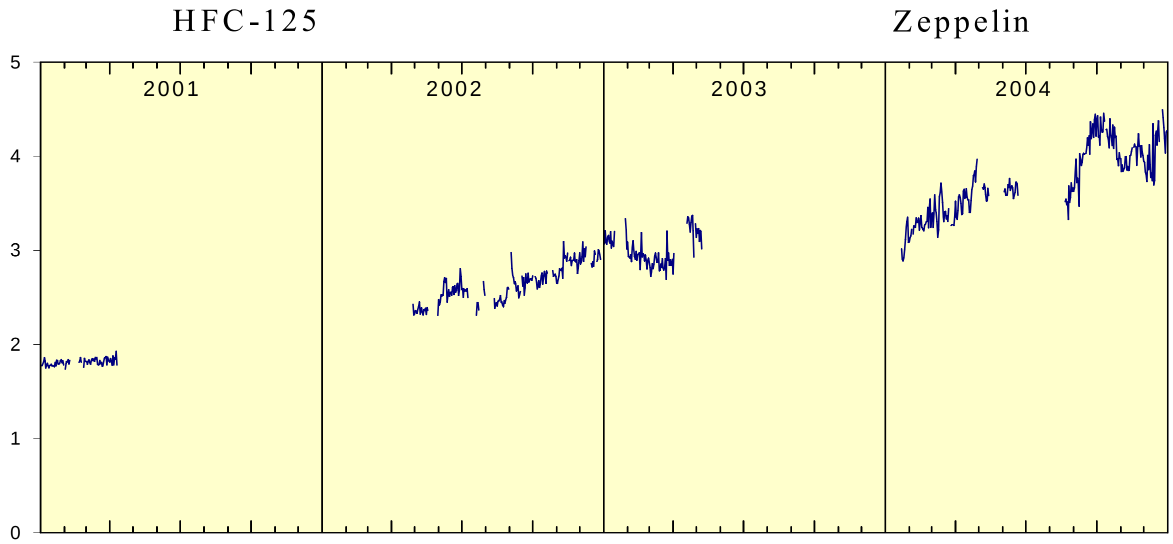
A.4 Hydrochlorofluorocarbons (HCFC)

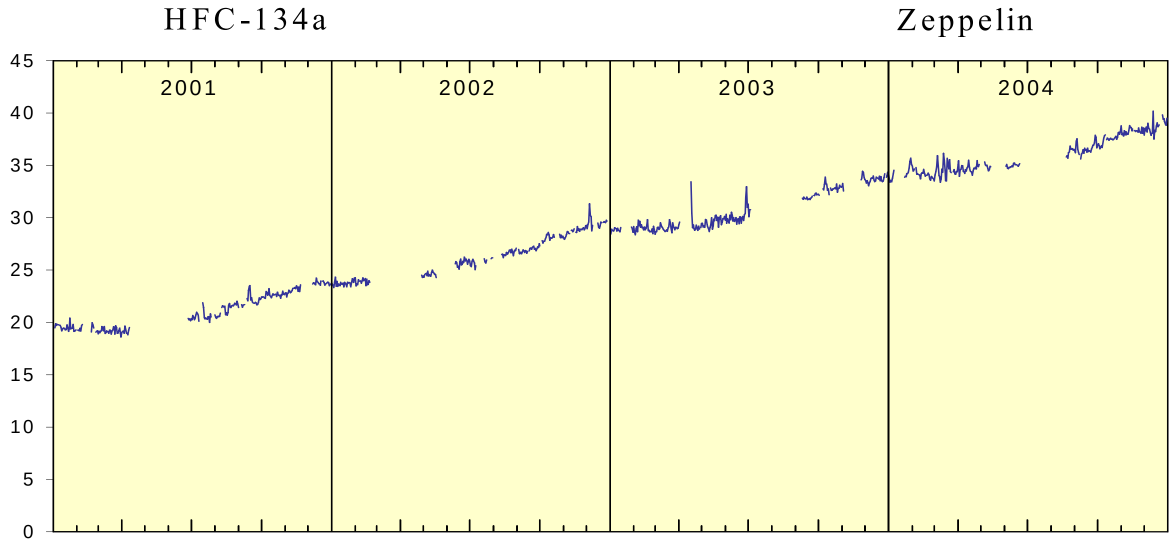


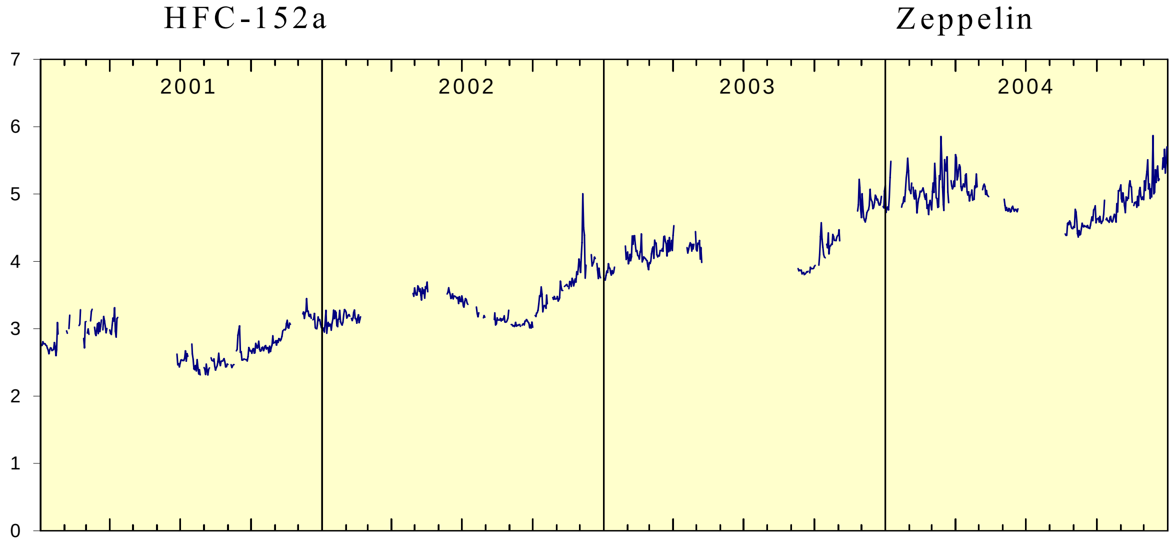




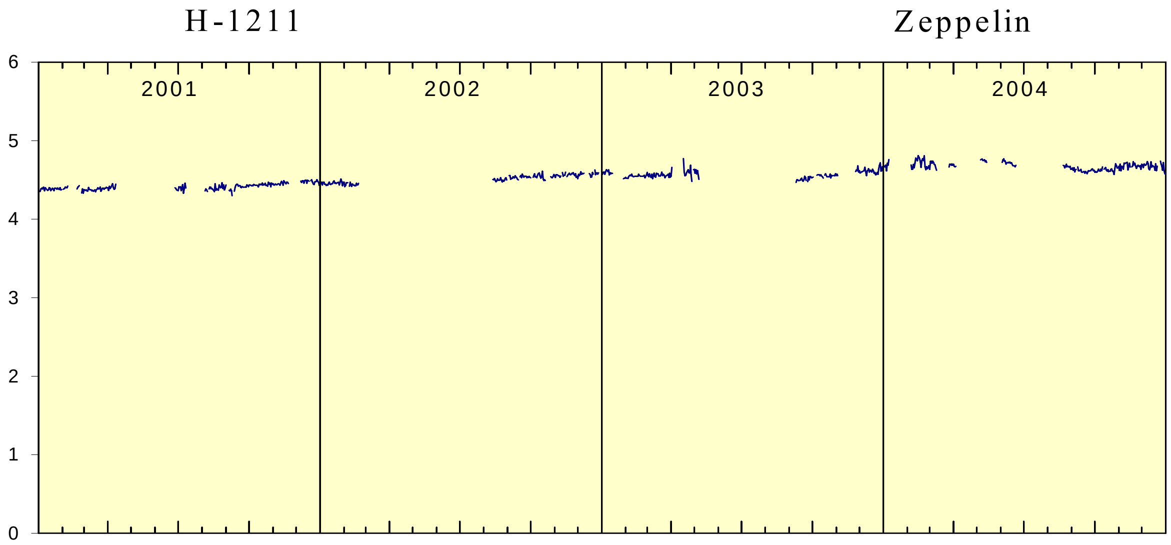
A.5 Hydrofluorocarbons (HFC)

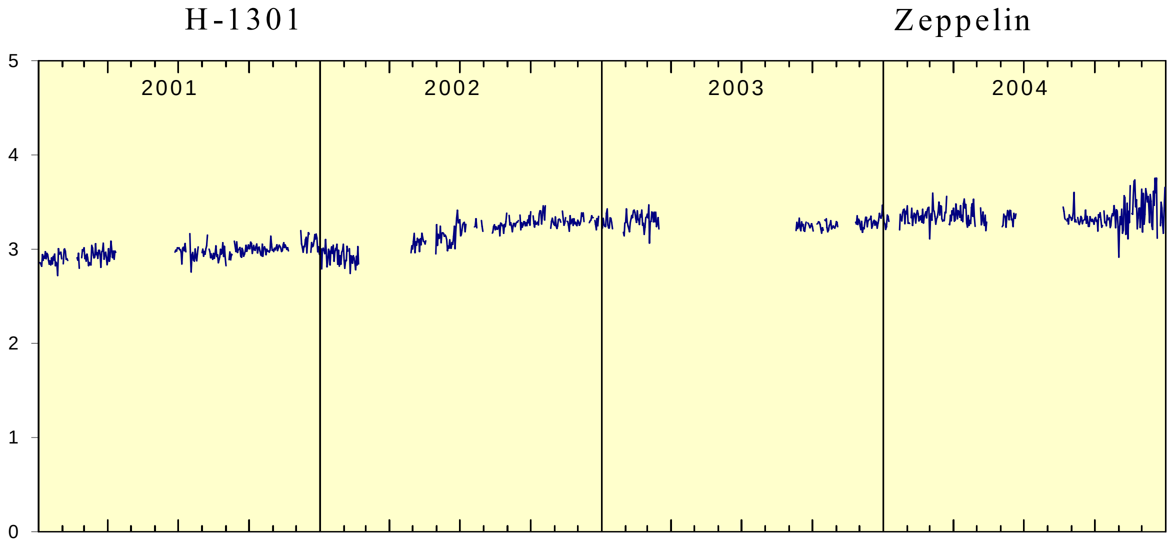




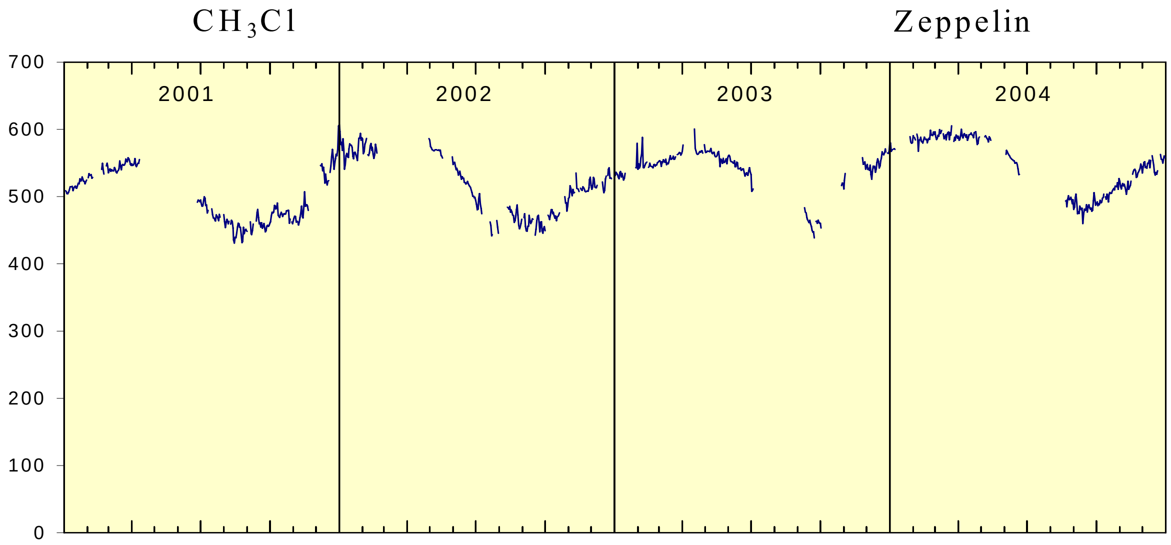


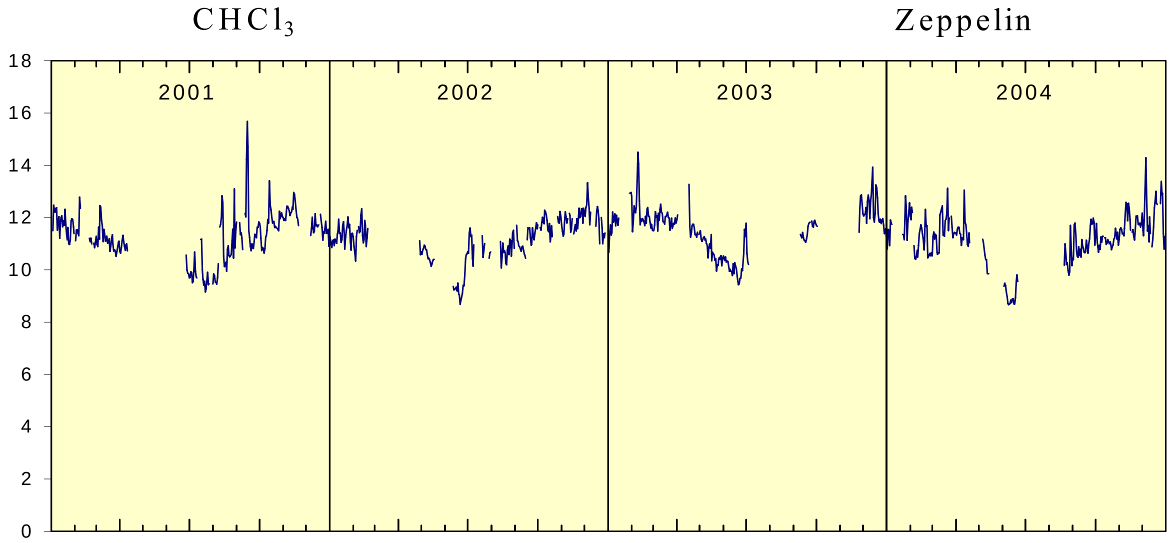
A.6 Halones

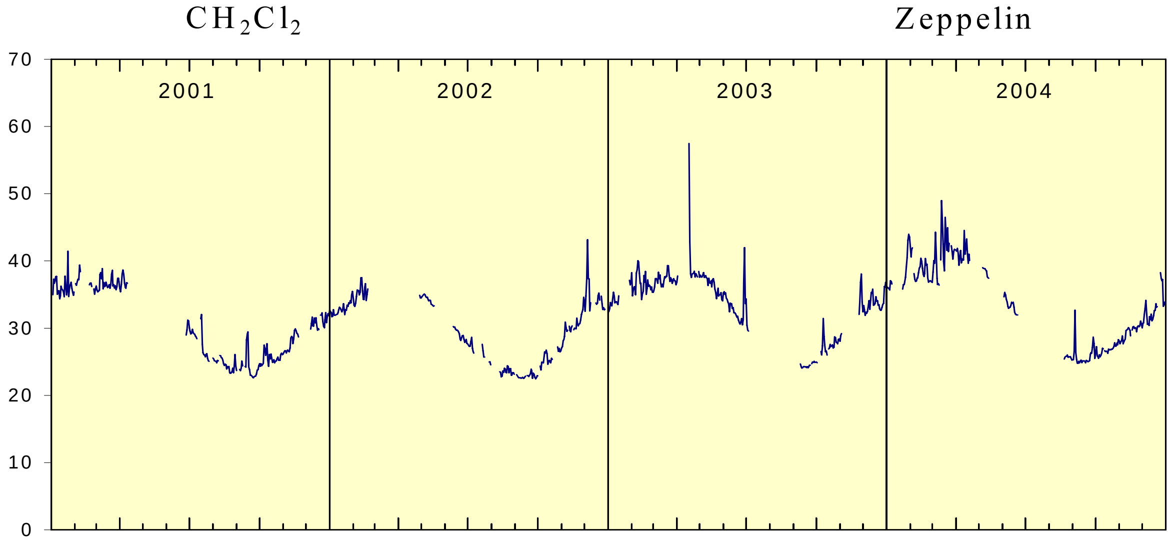

H-1211
Zeppelin
6
5
4
3
2
1
0
2001
2002
2003
2004

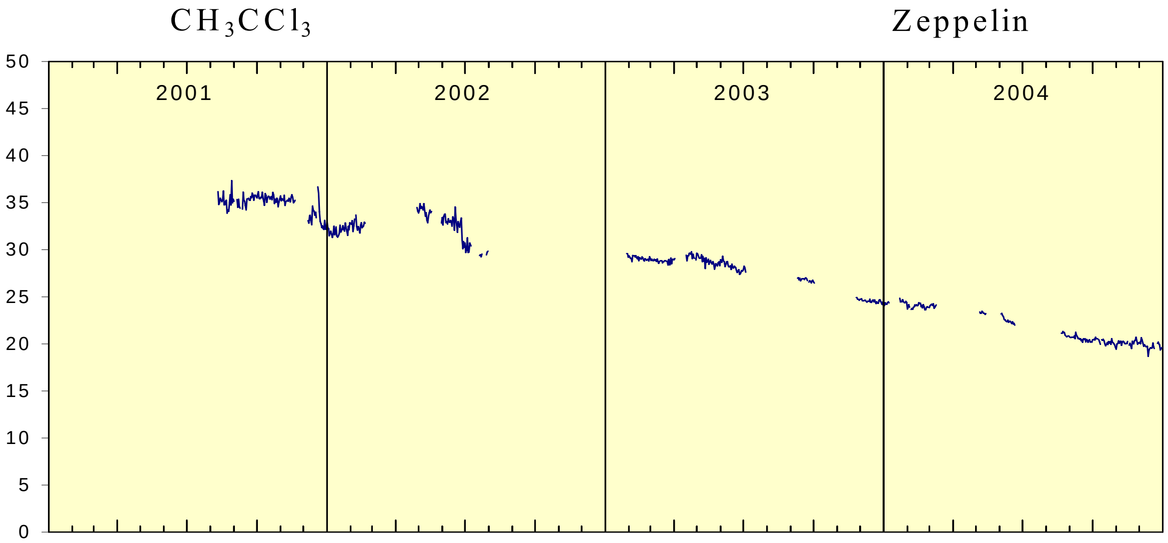

H-1301
Zeppelin
5
4
3
2
1
0
2001
2002
2003
2004

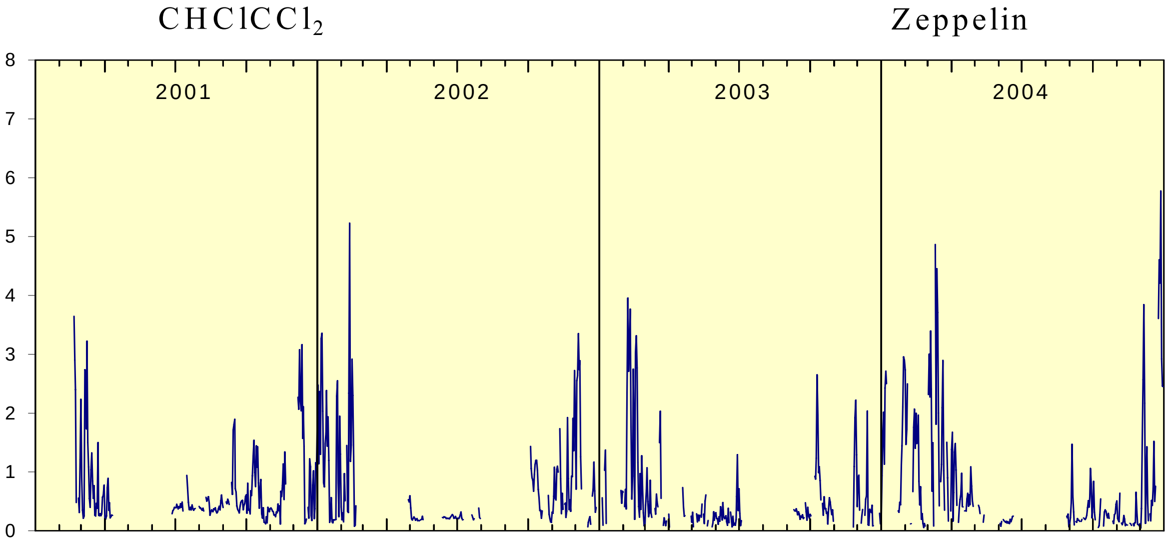
A.7 Chlorinated compounds

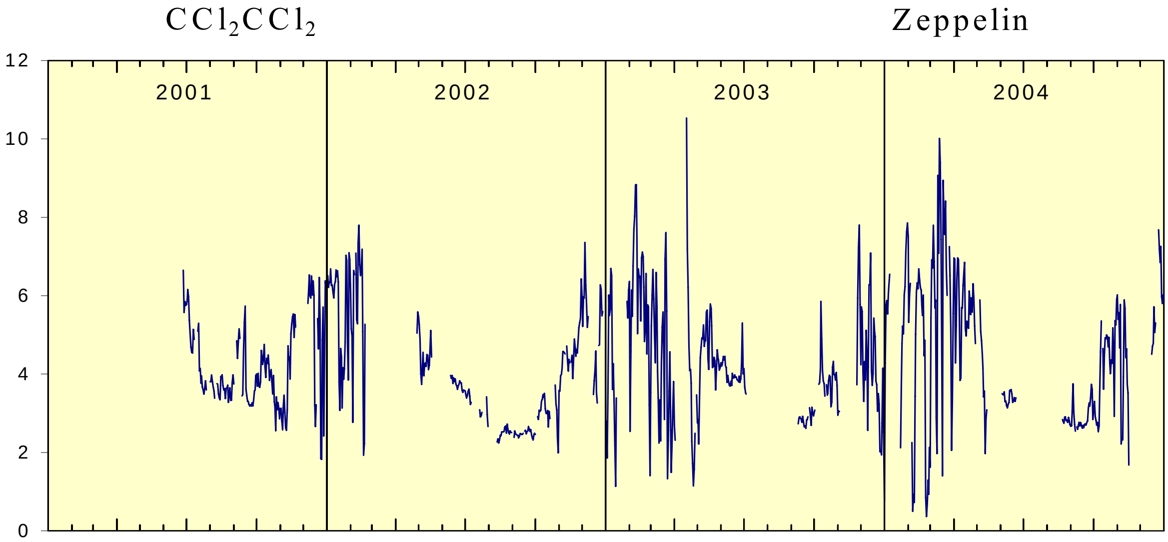




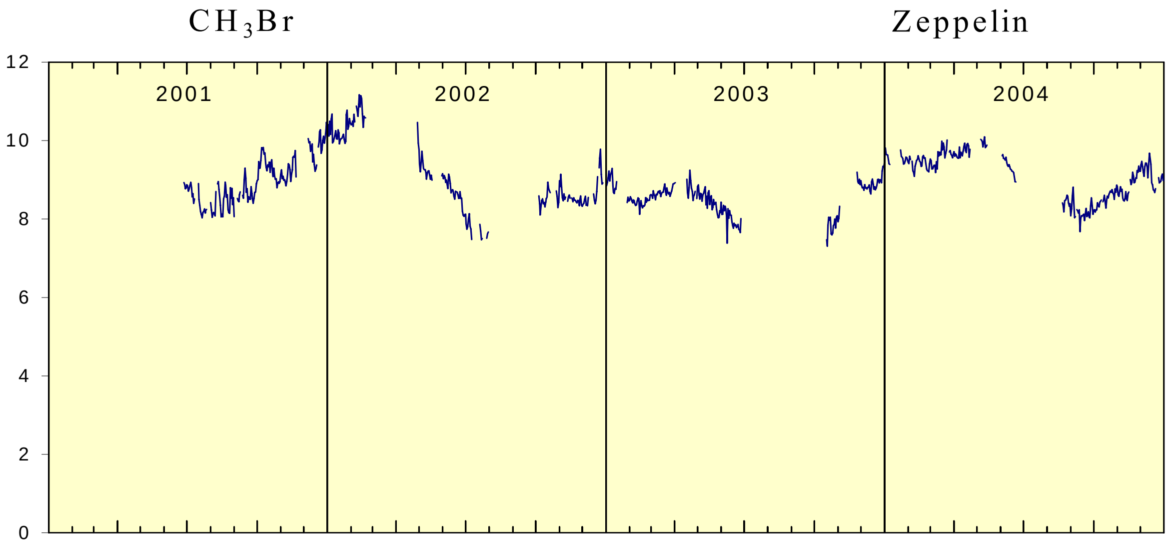


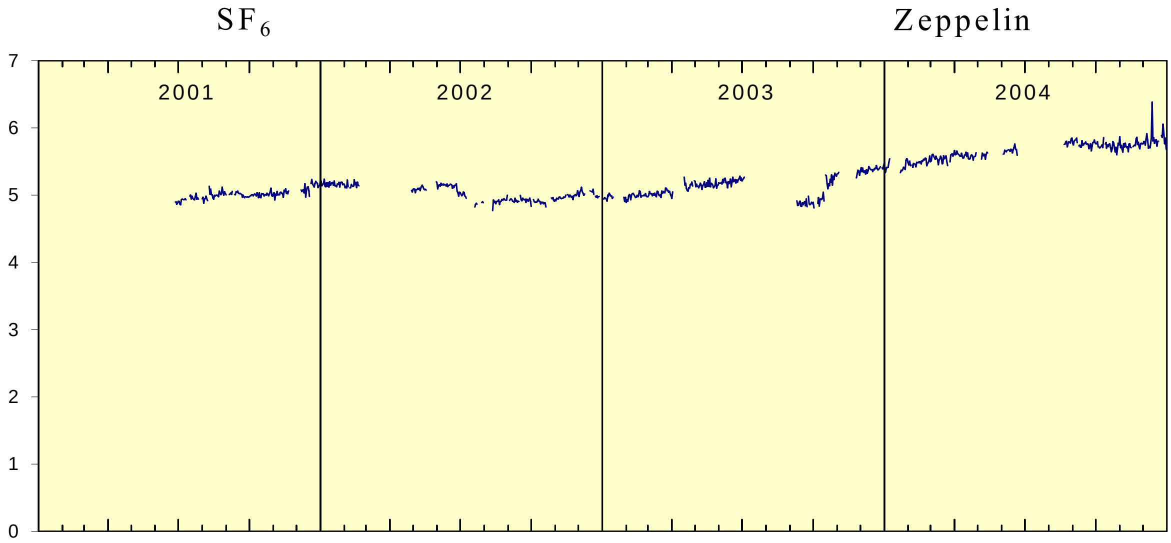

CH_3CCl_3
Zeppelin
50
45
40
35
30
25
20
15
10
5
0
2001
2002
2003
2004


$CHClCCl_2$
Zeppelin
8
7
6
5
4
3
2
1
0
2001
2002
2003
2004


CCl_2CCl_2
Zeppelin
12
10
8
6
4
2
0
2001
2002
2003
2004

A.8 Other halogenated compounds





Appendix B

Measurements

B.1 Instruments and methods

B.1.1 Halocarbons

To perform long-term high quality observations of volatile halocarbons at the Zeppelin station a specially designed instrument was installed in late spring 2000. The instrument currently monitors more than 20 compounds, including CFCs, HFCs, HCFCs, Halons and a range of other halogenated species. The gases monitored by the instrument are listed together with CH_4 and CO in table 2.

The instrument is a fully automated adsorption/desorption sampling device (ADS) coupled with an automatic gas chromatograph with a mass spectrometric detector (GC-MS). The system provides 6 air samples during 24 hours. The instrument is the same instrument as the ones located at the SOGE stations Mace Head and Jungfraujoch and all the five AGAGE sites. The four sites within the SOGE project are using calibration tanks, which are pressurized simultaneously at Mace Head and then calibrated to AGAGE (Advanced Global Atmospheric Gases Experiment) scale.

The instrument is remote controlled from NILU, but there is a daily inspection at the site from personnel from the Norwegian Polar Institute. There are about 4 to 6 visits from NILU each year for major maintenance work. All data are transferred to NILU on a daily basis. All data are processed by software, which is common for all AGAGE and SOGE stations.

There are some periods of missing during spring and summer due to instrumental problems, but the overall data coverage is still considered to be relatively good for the year 2004.

As member of the SOGE network and due to the good quality of data produced, the Zeppelin station is accepted as an associated member of the AGAGE network.

Results from the outlined trending methods are illustrated in Figure B.1 for HFC-134a for Zeppelin (2001-2003) where the panels show (a) The raw observed GC-MS data, (b) the baseline filtered data with trend curve and filter, (c) the algorithm derived growth rate in pptv/year and (d) %/year. Note that the annual yearly growth rate is not shown in this data, just the filtering results from the data using the 650-day smoothing after filtering of the seasonal cycle. The averaged seasonal cycle for HFC-134a for Zeppelin is shown in Figure B.2.

Measurement results for 2004 and trends based on the whole monitoring period 2001-2004 are shown in Table A.1, appendix A.1.
Measurement results for the whole monitoring period 2001-2004 are shown as plots in appendix A.

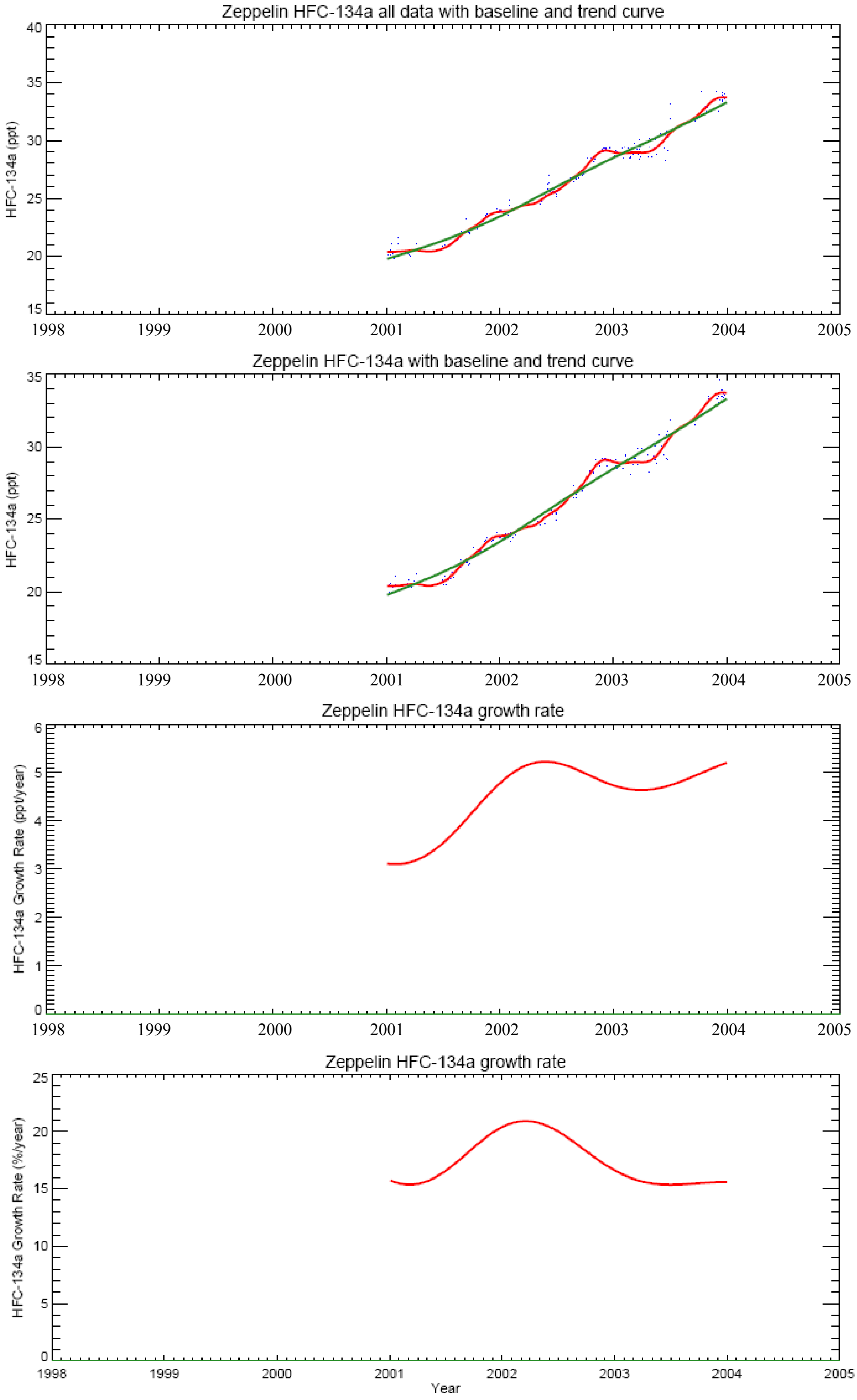


Figure B.1: Generation of trends in HFC-134a from observations at Zeppelin for 2001-2003. See text for panel description. Reproduced with permission, P.B. Krummel, CSIRO, Australia.

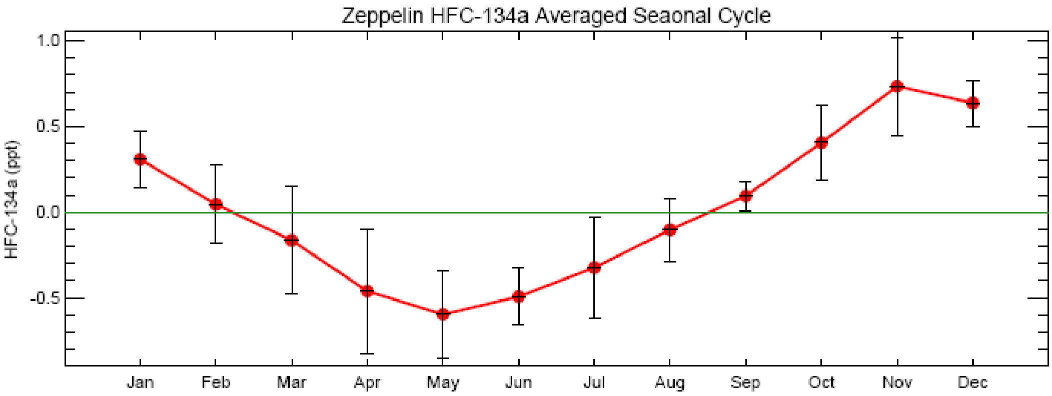


Figure B.2: Annually averaged (2001-2003) seasonal cycle for HFC-134a from GC-MS observations at Zeppelin. Reproduced with permission, P.B. Krummel, (CSIRO).

B.1.2 Methane

CH_4 is the second most significant greenhouse gas, and its level has been increasing since the beginning of the 19th century. Global mean concentrations reflect an annual increase, and the annual averaged concentration was 1782 ppb in 2001. The annual concentrations produce a peak in the northernmost latitudes and decrease toward the southernmost latitudes, suggesting significant net sources in northern latitudes.

The global growth rate is 8 ppb/year on average for the period 1984-2001, but the rates show a distinct decrease from the 1980s to 1990s. Growth rates decreased significantly in some years, including 1992, when negative values were recorded in northern high latitudes, and 1996, when growth almost stopped in many regions. However, both hemispheres experienced high growth rates in 1998, caused by an exceptionally high global mean temperature. And the global growth rates decreased again largely to record negative values in 2000 for the first time during the analysis period.

Monthly mean concentrations have a seasonal variation with high concentrations in winter and low ones in summer. Unlike CO_2 , amplitudes of the seasonal cycle are large for CH_4 not only in the Northern Hemisphere but also in southern high and mid-latitudes. In southern low latitudes, a distinct semi-annual component with a secondary maximum in boreal winter overlays the annual component. This is attributed to the large-scale transport of CH_4 from the Northern Hemisphere (GAW homepage).

At Mt. Zeppelin methane is monitored by the use of an automatic gas chromatograph with a flame ionisation detector (GC/FID). Air is sampled three times an hour and calibrated against an air standard once an hour.

The instrument produces a large amount of data requiring a specially made system for the extensive data handling. The installation of new data collection equipment was the first step to enable the methane data being processed by the same system as the halocarbon data. This data system is specially made at the Scripps Institution of Oceanography in California, but needs an upgrade before it can include the methane measurements. All methane data will be recalculated when this system is in place.

The instrument is quite old and there have been some problems with valve switching, detector function and the computer collecting the data. The problems increased over the year and in december 2004 the gas chromatograph broke down and had to be replaced. The instrument was dismantled and rebuilt to fit another type of chromatograph. Although the chromatograph has been replaced, valves and electronics have not. The equipment has by far exceeded its expected lifetime expectancy and should be replaced to avoid data loss and increasing maintenance costs. These problems have caused periods of reduced data availability. In consideration of these periods of data losses, the overall data coverage is still considered to be relatively good for the year 2004.

The instrument is calibrated against new traceable standards with references to standards used under the AGAGE programme. The last major audit was performed in September 2001 by personnel from the Swiss Federal Laboratories for Materials Testing and Research (EMPA) which is assigned by the World Meteorological Organization's (WMO) to operate the Global Atmospheric Watch (GAW) World Calibration Center for Surface Ozone, Carbon Monoxide and Methane. The results are published in EMPA-WCC report 01/3, concluding that methane measurements at the Zeppelin station can be considered to be traceable to the GAW reference standard. A new major audit will be performed in 2005. The continuous data are enhanced by the weekly flask sampling programme performed by NOAA CMDL. Figure B.3 shows nice correlation between the flask samples and the in situ measurements, both in seasonal variation and pollution events.

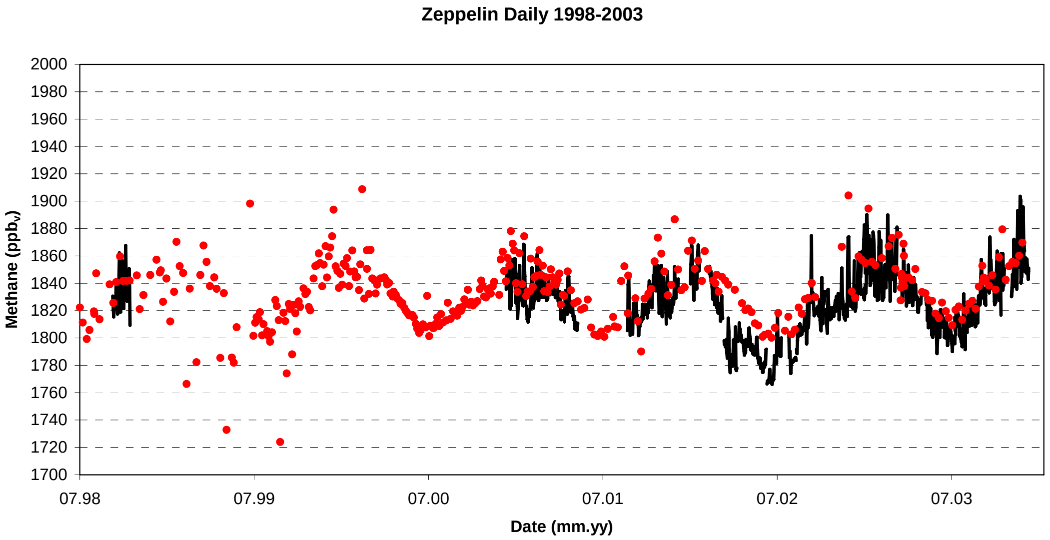


Figure B.3: Methane measurements at Mt. Zeppelin 1998 – 2003. Weekly flask samples (red dots) performed by CMDL compared with daily averaged in situ measurements (black line) performed by NILU.

All the flask data for Zeppelin and the daily mean of all data are plotted in Figure B.4 together with a fitted harmonic function. The blue function fitted to the flask data (red stars) has a gradient (methane concentration increase rate) of 3.63 ppb/year and crosses the y-axis in –5428 (i.e. x=0). The green function fitted to the daily mean data from Zeppelin (light blue cross) has a gradient of 3,21 and crosses the y-axis in –4609. The global growth rate of methane, determined using the measurements from the NOAA CMDL cooperative air sampling network, has since 2002 been between 1 and 5. The difference of the two curves is not constant, but in the region where they overlap, it is around 20 ppb. This system difference is comparable to other sites where both continuous and flask data are collected. Compared to the harmonic function fitted to the data (Figure B.5), there are 41 peaks that deviate more than 20 ppb from the function. In addition, in the period 1.4 –22.5 2002 the GC measurements are systematically lower than the function, and in the period 13.4-8.6 2003 the measurements are systematically higher than the function without crossing it. In the first period there is a deviation in the continuous data from the flask measurements, which we have not been able to explain. In the second period the continuous data are consistent with the flask measurements. The form of the harmonic function can be an artefact of the first period hence creating the deviation also in the second.

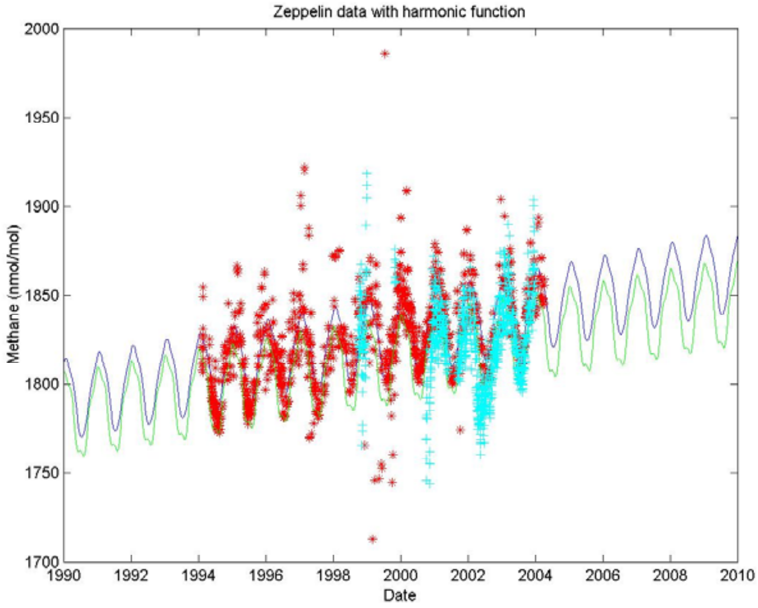


Figure B.4: Zeppelin flask data (red stars) with harmonic function (blue) together with GC daily mean data (light blue) with harmonic function (green) from year 1990 to 2010.

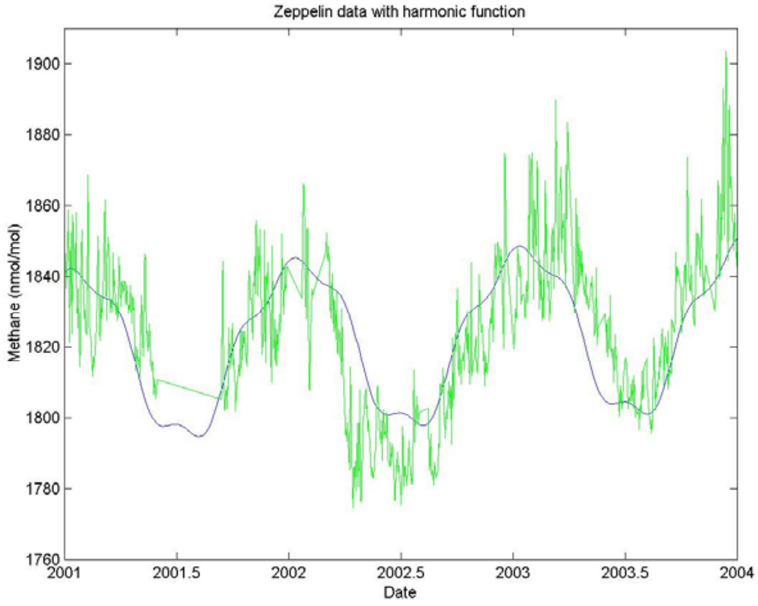


Figure B.5: Zeppelin GC data (green line) with harmonic function (blue) from 2001 to 2004.

When more data have been collected in a year, we expect to have a sufficient time series to allow fitting the harmonic function whist dropping the suspect data in April-May 2002. Year to year shifts in increase rates should then also be possible to extract from the record.

B.1.3 Carbon Monoxide

Tropospheric carbon monoxide CO is not a significant greenhouse gas, but brings about changes in the concentrations of greenhouse gases by interacting with hydroxyl radicals (OH). Concentrations of CO have increased in northern high latitudes since the mid-19th century, but have not changed significantly over Antarctica during the previous two millennia. The annual averaged concentration was about 93 ppb in 2001. The annual mean concentration is high in the Northern Hemisphere and low in the Southern Hemisphere, suggesting substantial anthropogenic emissions in the Northern Hemisphere.

Though the level of CO was increasing before the mid-1980s, the averaged global growth rate was -0.8 ppb/year for the period from 1992 to 2001. The variability of the growth rates is large. High positive growth rates and subsequent high negative growth rates were observed in northern latitudes and southern low latitudes from 1997 to 1999.

Monthly mean concentrations show a seasonal variation with large amplitudes in the Northern Hemisphere and small ones in the Southern Hemisphere. This seasonal cycle is driven by variations in OH concentration as a sink, emission by industries and biomass burning, and transportation on a large scale (GAW homepage).

CO is closely liked to the cycles of methane and ozone and like methane plays a key role in the control of the OH radical. Its emissions have influence on the increasing tropospheric ozone and methane concentrations.

The CO instrument at the Zeppelin station was reinstalled in September 2001. An international calibration during an audit from Swiss Federal Laboratories for Material Testing and Research (EMPA) was performed the same month to assess the quality of the measurements. EMPA represented the Global Atmosphere Watch (GAW) programme to include the measurements on the Zeppelin Mountain in the GAW programme. The results are published in EMPA-WCC report 01/3, concluding that methane measurements at the Zeppelin station can be considered to be traceable to the GAW reference standard.

The instrument is an automatic gas chromatograph with mercury oxide reduction followed by UV detection. It is performing analysis of 5 air samples and one standard within a time period of 2 hours. The standards are calibrated directly to a Scott-Marine Certificated standard and the Mace Head standards, which are related to the AGAGE-scale.

The instrument has been running without serious interruptions since installation. There is a period of missing data in late winter, due to computer problems. The overall data coverage is still considered to be quite good for the year 2004.

The continuous data are enhanced by the weekly flask sampling programme performed by NOAA CMDL. Figure B.6 shows nice correlation between the flask samples and the in situ measurements, both in seasonal variation and pollution events (e.g. Dec. 2002).

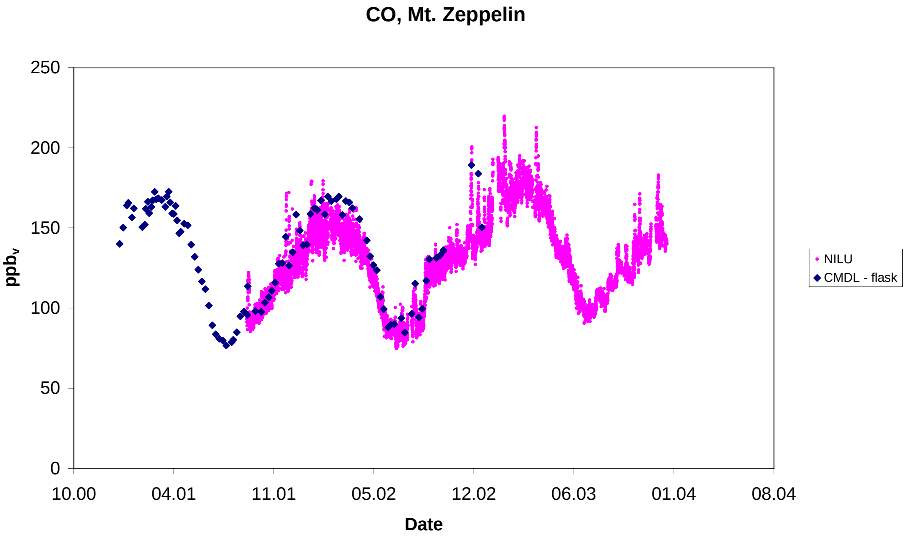


Figure B.6: CO measurements at Mt. Zeppelin 2001 – 2003. Weekly flask samples performed by CMDL compared with hourly in situ measurements performed by NILU.

B.1.4 The WMO GAW precision filter radiometer at Ny-Ålesund

The Integrated Global Observing Strategy (IGOS), which is a partnership of international observations, recently presented an atmospheric chemistry theme report (2004) with focus on the four grand challenges in atmospheric chemistry; the tropospheric air quality, the oxidation efficiency of the atmosphere, the stratospheric chemistry and ozone depletion, and the chemistry – climate interactions. Aerosols are important within all these four fields. At ground level the effects of anthropogenic PM smaller than 2.5 upon human health is well documented while the effect of aerosol/gas interactions on the tropospheric air quality and the oxidation capacity are not yet fully understood. Tropospheric aerosols cause a direct radiative forcing by scattering and absorbing solar radiation and indirectly by changing the radiative properties of clouds. Dependant on the aerosols' physical and chemical characteristics they may either reflect radiation, e.g. as white sulphates are thought to do, or they may absorb radiation, e.g. as black carbon particles will do. The magnitude of the total forcing remains unknown. In the stratosphere gas-particle interactions can affect the chemistry that controls the ozone layer.

Satellites are becoming increasingly important for measuring total vertical aerosol columns and vertical profiles. Ground based networks are nevertheless very important and necessary, both with respect to verification of satellites and for filling in gaps in the space based remote monitoring of aerosols. The precision filter radiometer (PFR) instrument at Ny-Ålesund is part of a small WMO GAW trial network, and is now operating on it is fourth year. A brief summary of the first three years is given below.

Figure B.7 presents the aerosol optical density at 501 nm at Ny-Ålesund. As seen the AOD are higher during the Arctic spring compared to the measurements during summer. This is due to the Arctic haze phenomenon in the boundary later, and the suppression of removal mechanism during winter and early spring due to strong inversions. During summer precipitation removes the aerosols as well as water-soluble gases. As seen from Figure B.7 there is no indications of a trend in the results from one year to the next, and the variation from one day to the next can be quite high.

There are a large number of days without results in Figure B.7. The main problem is that clear sky conditions are needed for having a valid result and that clouds frequently occur at Spitsbergen. There is also more frequent cloudy or foggy conditions near the ground in Ny-Ålesund than at higher levels. After three years with measurements there is therefore a strong desire to move the measurement from the present location in Ny-Ålesund up to the site at Zeppelin Mountain. This will give more valid results, but also raises a need for a sun tracker at the Zeppelin site. The funding is, however, at present missing. A second problem at the current location is a drift in the pointing of the PFR instrument that caused periods of rejected data. The cause of this drift is not yet identified, and data still have to be rejected in periods before corrections of the pointing can be made.

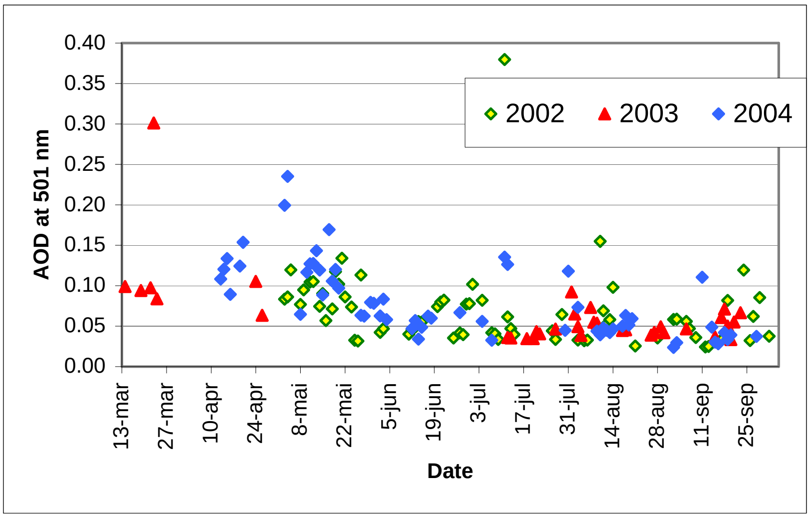


Figure B.7: Aerosol optical depth at 501 nm measured in Ny-Ålesund during three years.

Figure B.8 presents Ångström's alpha from his empirical formula for the wavelength dependence of the total haze scattering, $\sigma_A \sim \lambda^{-\alpha}$, where σ_A is the total fraction of light scattered by the particles within 1 cm^3 at the light wavelength λ. The exponent α is Ångström's alpha. The index "A" in σ_A means scattering by aerosols.

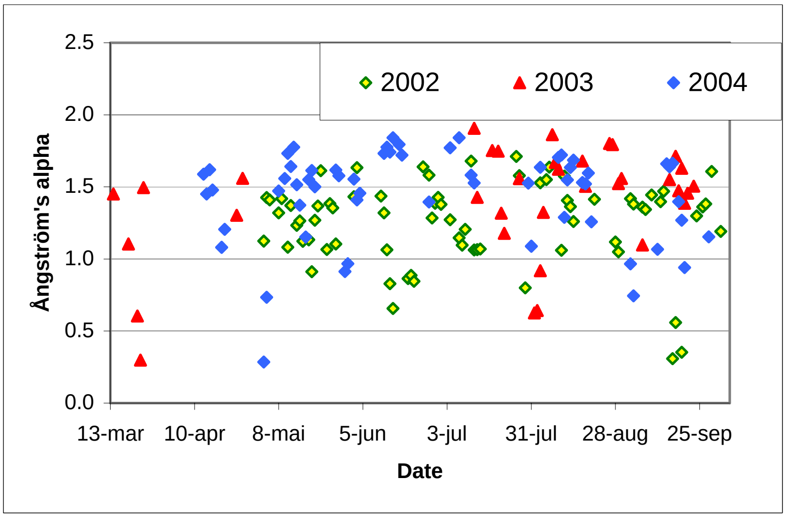


Figure B.8: Ångström's alpha measured in Ny-Ålesund.

The PFR instrument measures the total extinction of sunlight, and the extinction due to particles, or aerosol optical depth, is calculated as the difference between the total extinction and molecular scattering and ozone absorption at some wavelengths. The scattering due to molecules and absorption due to ozone can be calculated. The alpha exponent varies mostly between 0.8 and 1.9 in Ny-Ålesund.

Appendix C

Calculation of Trends

C.1 GC-MS *in situ* observations

Under the SOGE project, and as associated network to the AGAGE network, all SOGE data produced during it project has been processed in the AGAGE system to provide long term trends for the different species measured.

The method used to drive long term trends entail:

a. Deriving a baseline and pollution (i.e. above-baseline elevations) delineation of the raw GC-MS data for the selected period using a statistical filtering algorithm developed under the AGAGE program at Georgia Institute of Technology, USA.
b. From the baseline data, aggregate data into monthly mean concentrations (Figure C.1).
c. The baseline is filtered to remove outliers and seasonal cycles to generate a smoothed baseline for trend analysis using a 650 day moving average harmonics/polynomial fit algorithm developed by CSIRO, Australia as part of AGAGE methodology (Figure C.2).
d. The detrending of the baseline by harmonics allows the generation of the seasonal cycle of each measured compound per year of data, which is then aggregated to develop an annually averaged seasonal cycle for each compound per station (Figure C.3).

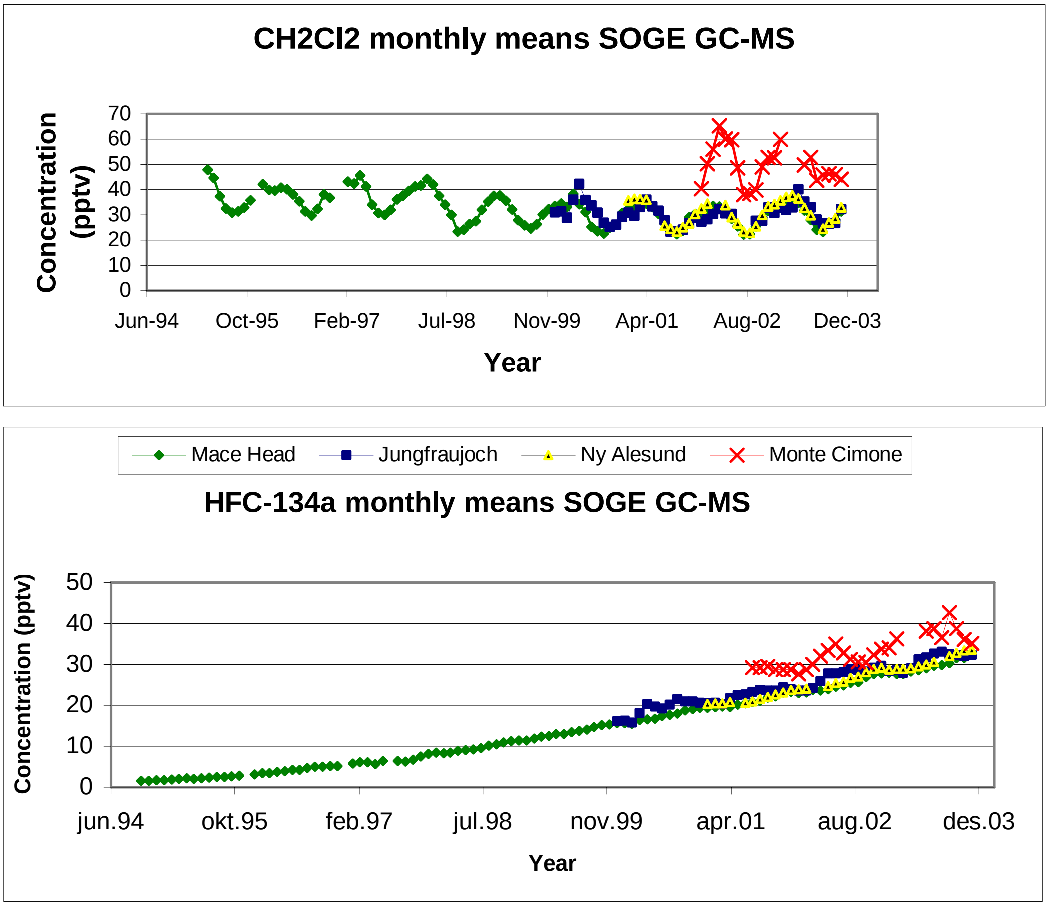


Figure C.1: Monthly mean baseline filtered concentrations from all 4 SOGE GC-MS stations for (a) CH_2Cl_2 and (b) HFC-134a. Data reproduced with permission, R.H.J Wang (Georgia Tech., USA).

Figure C.1 illustrates the monthly mean baseline results for the SOGE GC-MS observations. The stations at the fringe of Europe (Mace Head, Ireland and Ny-Ålesund, Spitsbergen) show lower monthly average baselines than the central Western Europe stations at Jungfraujoch (Switzerland) and Monte Cimone (Italy). The magnitude of the baseline at the Italian station is due to the proximity to European source regions. Another important consideration is that the Georgia Tech data filter relies upon observations showing baseline periods in order to decouple the baseline from observed pollution events. The Swiss and Italian stations, although better positioned to observe emissions from sources, are less suited for defining a European baseline. Conversely, the Irish and Norwegian stations are better placed as background stations.

Results from the outlined trending methods are illustrated in Figure C.2 for HFC-152a for Zeppelin station (from 2001-2003) where the panels show (a) The raw observed GC-MS data, (b) the baseline filtered data with trend curve and filter, (c) the algorithm derived growth rate in pptv/year and (d) %/year. Note that the annual yearly growth rate is not shown in this data, just the filtering results from the data using the 650-day smoothing after filtering of the seasonal cycle. The averaged seasonal cycle for HFC-152a for Zeppelin is shown in Figure C.3, clearly showing the spring maximum and summer minima associated with a compound whose predominant removal processing in the atmosphere is reaction with the OH radical.

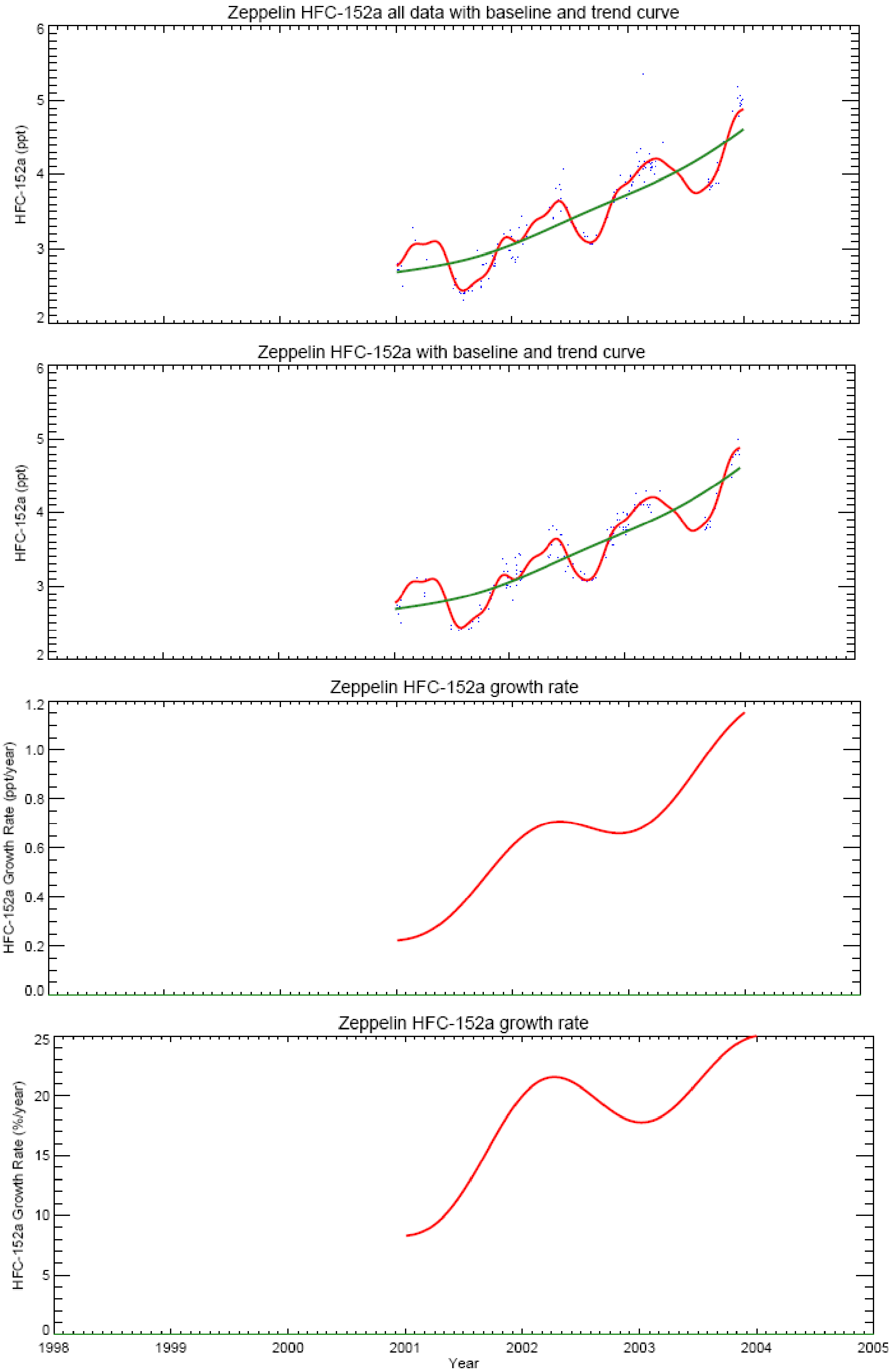


Figure C.2: Generation of trends in HFC-152a from observations at Zeppelin station for 2001-2003. See text for panel description. Reproduced with permission, P.B. Krummel, CSIRO, Australia.

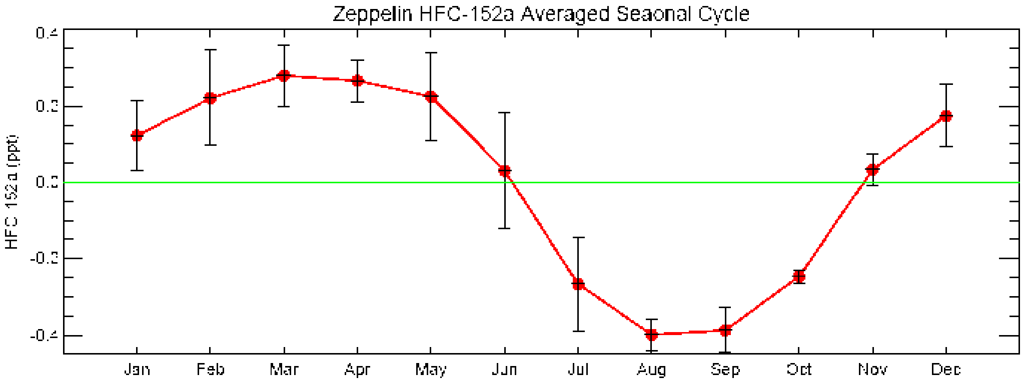


Figure C.3: Annually averaged (2001-2003) seasonal cycle for HFC-152a from GC-MS observations at Zeppelin station. Reproduced with permission, P.B. Krummel, (CSIRO).

Annual growth rate estimates based on observations at SOGE GC-MS stations are illustrated in Figure C.4–Figure C.6. Each estimate (shown as % per year per station) is generated by aggregation of the monthly mean baseline into a yearly estimate. Also shown for reference is an annualised average concentration for each compound observed for each station. The trends illustrated for HFC-134a (Figure C.4) show that historically this compounds growth rate is slowing at Mace Head and that during the SOGE period the growth rate is consistent between observation stations and has slowed from 2000-2003.

Figure C.5 shows that the rate of growth in the HFC-152a baseline has increased over the period of SOGE observations (2001-2003). The growth rate was significantly greater in 2002 at all 4 SOGE GC-MS observation sites. This has also been shown in the emission estimates for Mace Head where the source strengths clearly have increased for HFC-152a. Again, the annual average baseline for Monte Cimone and Jungfraujoch is higher than other SOGE sites.

Declining European emissions have been observed for most anthropogenic chlorocarbons, illustrated in Figure C.6 for CH_3CCl_3. Such reductions are in-line with long-term AGAGE observations for this compound, whose atmospheric concentrations will continue to decline, as it is no longer emitted to any significant extent. The slowing of the rate of decline is also expected as its reaction with OH removes residual CH_3CCl_3 from the global atmosphere. Recent European emission estimates for CH_3CCl_3 based on observations at Jungfraujoch and Mace Head are the subject of a manuscript under review at the journal Nature, with a further publication planned to include all SOGE observations.

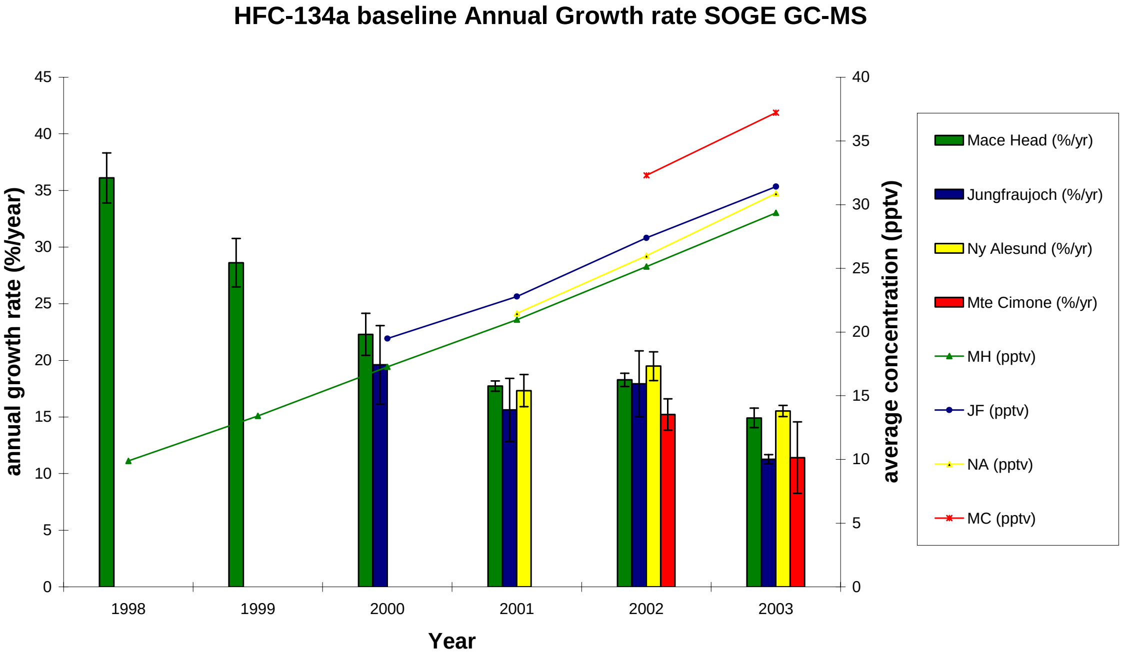


Figure C.4: Growth rate trends for HFC-134a from SOGE GC-MS observations 1998-2003.

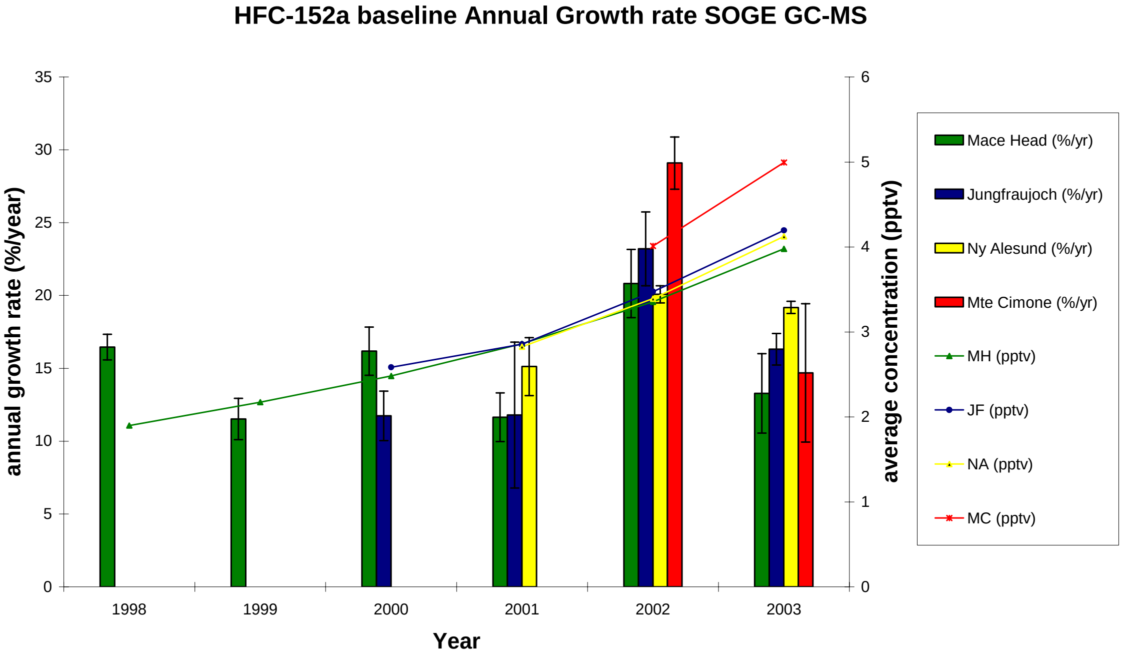


Figure C.5: HFC-152a annual growth rate derived from GC-MS observations.

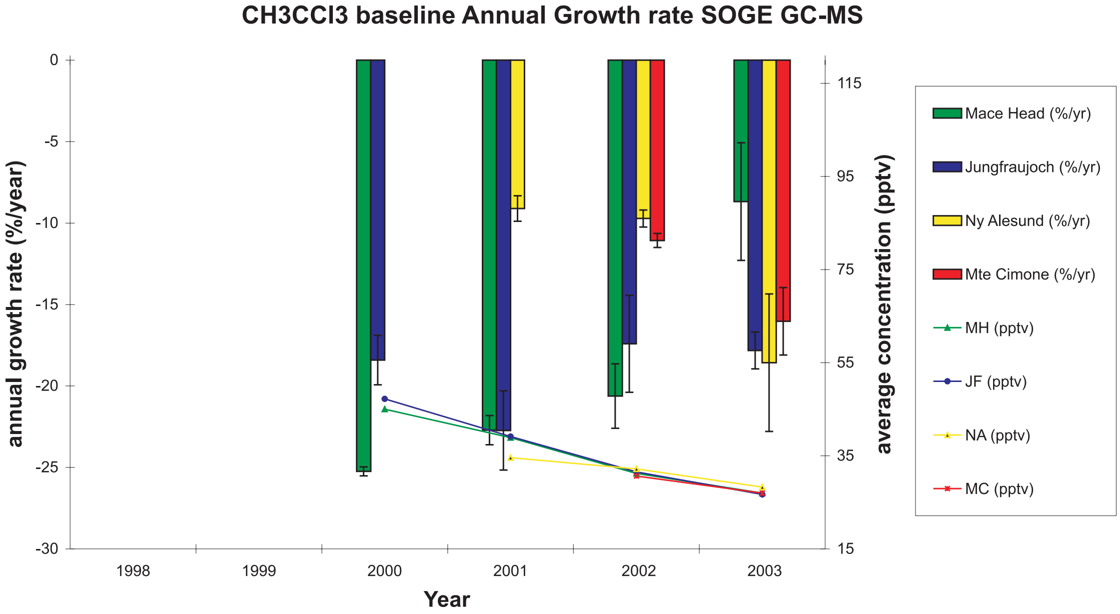


Figure C.6: Decline observed in CH_3CCl_3 baselines 2000-2003 at SOGE GC-MS sites.

A summary of available trends derived from *in situ* GC-MS observations under SOGE and total column FTIR observations (in Ny-Ålesund performed by Alfred Wegner Institute, Germany) is included in Table C.1 below. The growth rates shown are an average of the yearly growth rates for the SOGE period listed (mostly 2001-2003) but longer trend records are listed for Mace Head and Jungfraujoch (pre SOGE data). The listed average includes all periods, hence whilst e.g. CFC-12 at Mace Head is recently declining, the long term trend (1994-2003) is still positive.

It is very important to note that the length of the available data record for each station will reflect in the quality of the trends data, given that the algorithms used to derive baselines, elevations, and smoothing have been developed for long-term observation sites in AGAGE (1978 to date). Hence, for example, the trends generated for Monte Cimone (as the most recently equipped station) are right on the lower limit of what can be usefully used to determine accurate trend information (650 day smoothing). In addition, losses of data due to mechanical failure of the monitoring equipment or poor quality data, which has to be removed, will also adversely affect the accuracy of the long term trend derivations. Conversely, the longer the data record that is available, the more accurate the trending algorithm becomes. Future continuation of *in situ* GC-MS observations and subsequent quality control filtering should enable more reliable trend estimations.

Table C.1: Summary of all available trends. N/A stands for "Not Applicable".

#	SPECIES	**Mace Head**, Ireland	**Jungfraujoch**, Switzerland	**Ny-Ålesund**, Spitzbergen	**Mte Cimone**, Italy	**Ny-Ålesund,** Spitzbergen	**Jungfraujoch,** Switzerland
		in situ GC-MS (ppt/yr)*, (%/yr)* (period)	*in situ* GC-MS (ppt/yr)*, (%/yr)*, (period)	*in situ* GC-MS (ppt/yr)*,(%/yr)*, (period)	*in situ* GC-MS (ppt/yr)*,(%/yr)*, (period)	Total columns, FT-IR (ppt/yr), (%/yr)	Total columns FT-IR (molec/cm^2)
1	HFC-125	+0.39 (+20.38%) (1998-2003)	+0.42 (+18.52%) (2000-2003)	+0.74 (+34.92%) (2001-2003)	+0.60 (+18.68%) (2002-2003)	N/A	N/A
2	CFC-115	+0.04 (+0.53%) (1998-2003)	-0.04 (-0.49%) (2000 2003)	+0.17 (+2.00%) (2001-2003)	-0.14 (-1.74%) (2002-2003)	N/A	N/A
3	Halon-1301	+0.06 (+1.97%) (1998-2003)	+0.03 (+1.00%) (2000-2003)	+0.12 (+3.98%) (2001-2003)	+0.02 (+0.44%) (2002-2003)	N/A	N/A
4	HFC-134a	+3.98 (+23.0%) (1998-2003)	+3.95 (+16.11%) (2000-2003)	+4.53 (+17.45%) (2001-2003)	+4.57 (+13.31%) (2002-2003)	N/A	N/A
5	HFC-152a	+0.42 (+14.98%) (1998-2003)	+0.53 (+15.76%) (2000-2003)	+0.63 (+18.13%) (2001-2003)	+0.94 (+21.89%) (2002-2003)	N/A	N/A
6	HCFC-22	+4.65 (+3.02%) (1999-2003)	N/A [a]	+5.22 (+3.15%) (2001-2003)	+2.01 (+1.16%) (2002-2003)	+6.0 (+4.13%) (1992-2002)	+6.33E13 +2.9 %/yr (1999-2003)
7	CFC-12	+0.13 (+0.33%) (1994-2003)	+1.80 (+0.34%) (2000-2003)	+5.74 (+1.04%) (2001-2003)	-7.17 (-1.28%) (2002-2003)	Nearly constant over the last four years	-3.14E12 -0.04%/yr (1999-2003) Not statistically defined
8	HCFC-124	+0.09 (+6.79%) (1998-2003)	+0.08 (+5.25%) (2000-2003)	+0.12 (+7.22%) (2001-2003)	N/A	N/A	N/A
9	HCFC-142b	+0.83 (+6.19%) (1998-2003)	N/A [a]	+0.72 (+4.75%) (2001-2003)	N/A [c]	N/A	N/A
10	CH_3Cl	-6.33 (-1.15%) (1998-2003)	-4.06 (-0.74%) (2000 2003)	+6.67 (+1.32%) (2001-2003)	-21.06 (-3.77%) (2002-2003)	Not available	Not available
11	CFC-114	-0.03 (-0.16%) (1998-2003)	-0.06 (-0.34%) (2000 2003)	+0.02 (+0.10%) (2001-2003)		N/A	N/A
12	Halon-1211	+0.07 (+1.66%) (1998-2003)	+0.09 (+2.17%) (2000-2003)	+0.07 (+1.51%) (2001-2003)	-0.05 (-1.07%) (2002-2003)	N/A	N/A
13	CH_3Br	-0.49 (-5.28%) (1998-2003)	-0.61 (-5.83%) (2000 2003)	+0.14 (+1.64%) (2001-2003)	+0.36 (+4.06%) (2002-2003)	N/A	N/A
14	HCFC-123	+0.01 (+12.45%) (1999-2003)	N/A [b]	N/A [b]	N/A [b]	N/A	N/A
15	CFC-11	-1.54 (-0.58%) (1994-2003)	-2.07 (-0.80%) (2000 2003)	+0.07 (+0.02%) (2001-2003)	-4.50 (-1.72%) (2002-2003)	Not available yet	Not available yet
16	HCFC-141b	+1.42 (+10.2%) (1998-2003)	+0.90 (+5.07%) (2000-2003)	+1.28 (+7.38%) (2001-2003)	N/A [c]	N/A	N/A
17	CH_2Cl_2	-1.17 (-3.39%) (1998-2003)	-0.09 (-0.28%) (2000 2003)	+0.08 (+0.24%) (2001-2003)	-1.69 (-3.34%) (2002-2003)	N/A	N/A
18	CFC-113	-0.52 (-0.64%) (1994-2003)	-0.52 (-0.64%) (2001 2003)	+0.81 (+0.99%) (2001-2003)	N/A	N/A	N/A
19	$CHCl_3$	-0.14 (-1.14%) (1994-2003)	-0.27 (-2.82%) (2000 2003)	+0.13 (+1.15%) (2001-2003)	-0.90 (-7.80%) (2002-2003)	N/A	N/A
20	CH_3CCl_3	-11.0 (-16.91%) (1994-2003)	-6.96 (-19.09%) (2000-2003)	-3.82 (-12.47%) (2001-2003)	-3.85 (-13.55%) (2002-2003)	N/A	N/A
21	CCl4	-1.00 (-1.01%) (1994-2003)	+2.61 (+2.67%) (2000-2003)	+0.30 (+0.32%) (2001-2003)	N/A [d]	Not available	Not available yet
22	$CHClCCl_2$	-0.07 (-5.67%) (1998-2003)	-0.27 (-16.69%) (2000-2003)	N/A	N/A	N/A	N/A
	SF_6	N/A	N/A	N/A	N/A	+0.31±0.08 (1993-2002)	+2.55E12 +(0.24±0.01) ppt/yr (1993-2002)

Notes: * The *in situ* trend (in ppt/year) is the instantaneous growth rate and is calculated by taking the first derivative of the long-term trend curve (TR). The long term trend curve data is calculated with 650 day smoothing of the baseline selected data (baseline as defined by AGAGE/Georgia Tech filtering algorithms) with harmonics removed. All of the above are calculated as daily values and the annual values are simply the average of the daily values for each year. Presently there is insufficient long term data to accurately apply this technique to the Ny-Ålesund or Monte Cimone SOGE datasets with the same confidence as for the Mace Head and Jungfraujoch stations. Reproduced with permission of Paul Krummel, CSIRO, Australia.

a. In situ measurements compromised by foam blowing agents used in lift shaft construction

b. Below instrument limit of detection

c. Data for HCFC-142b and HCFC-141b at Monte Cimone is irregular in terms of it's baseline determination. Using the algorithm, the growth rates are both negative. The negative values are distortions due to the lack of baseline periods and close proximity to source regions. Longer time series may allow more accurate trends to be determined at Monte Cimone for these species.

d. Data quality and baseline poor for Monte Cimone site

Appendix D

Indirect methods for quantification of emissions

D. Indirect methods for quantification of emissions

Most Kyoto greenhouse gases (GHG) are currently observed in the atmosphere. Their concentrations depend on levels of emissions, and hence GHG emissions can be studied from their observed concentration. Figure D.1 shows an example of measured time series of one of the Kyoto GHG gases, HFC-125, at four observational sites in Europe (part of the network SOGE, System for Observation of halogenated Greenhouse gases in Europe).

The results reflect that different air masses arriving at the measurement sites are polluted with HFC-125 to a variable extent. HFC-125 is removed from the atmosphere very slowly. Once emitted into the atmosphere it will accumulate and mix globally as it is transported around the world by the wind systems. The observations show a baseline representing air masses that have not been influenced be emissions recently, reflecting a global average background level. As HFC-152 is currently emitted at a rate that is higher than the rate of removal from the atmosphere, the background concentration is increasing.

Superimposed on the baseline is a series of spikes, representing air masses that have more recently been exposed to emissions. The spikes arrive at the four stations at different times, according to the variations in the wind systems. Typically the spikes are higher at the locations that are closer to the high emission regions (higher at Jungfraujoch, Switzerland and Monte Cimone, Italy than at Mace Head, Ireland and Ny-Ålesund, Spitsbergen) as the high concentrations near the emissions are diluted during transport to more remote areas.

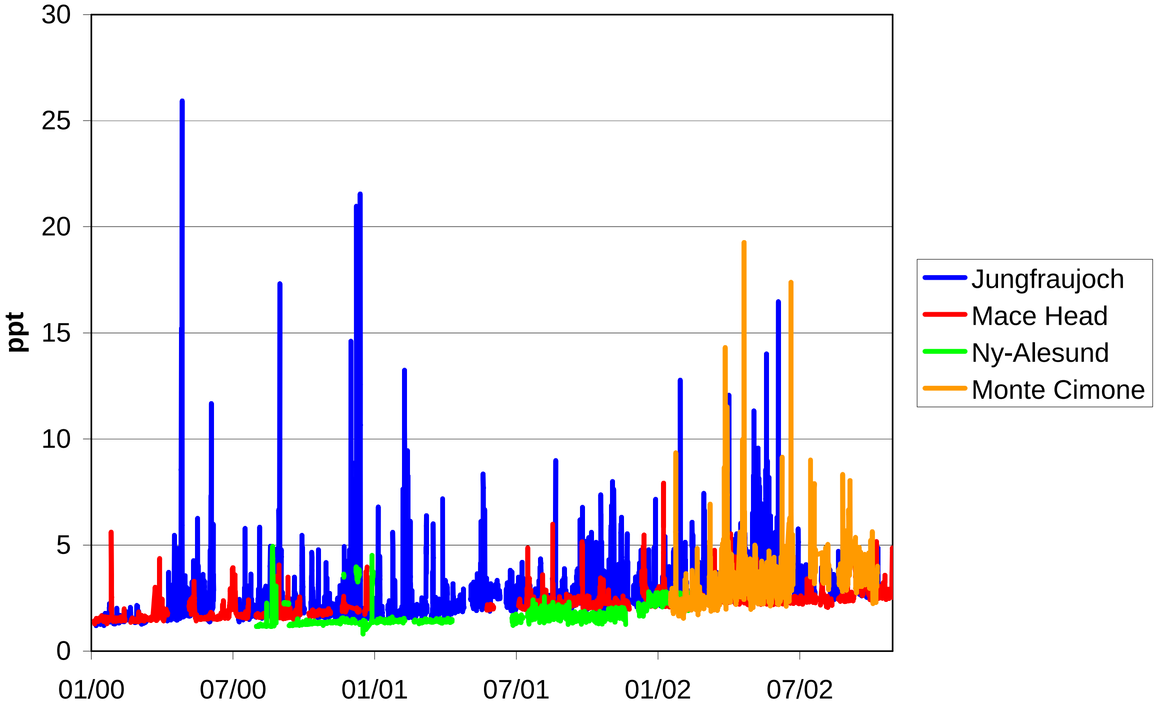


Figure D.1: Data series of HFC-125 at four observational sites in the European SOGE network.

In general and in principal, results as depicted in Figure D.1 can be used to deduce information on emissions in two ways. First, the baseline can be used to deduce global emissions as it represents a global background concentration. Second, the spikes can be used to deduce regional emissions, when coupled to other information, as meteorological data that can be used to determine the history of the air masses arriving at the stations. On this background, various tools and approaches used to study emissions of Kyoto GHG based on observed concentrations in the atmosphere will be presented and discussed.

D.1 General approach

Determining emissions from observed concentrations requires knowledge about the processes governing the distribution of the GHG in the atmosphere. The processes can be described in various kinds of numerical models. A combination of observations and modelling results are needed in the estimation of the emissions.

When it comes to processes, firstly one needs to know the sinks of the gas to take into account losses underway from the location of the emissions to the sites of observations. For SF_6, PFC, most HFCs and N_2O such losses can usually be neglected as they are very slow and take place at high levels in the atmosphere. CH_4 on the other hand is removed from the atmosphere by reaction with the hydroxyl radical, OH. Depending on the application this loss needs to be taken into account in indirect estimation of methane emissions. Much more complex is the situation for CO_2, which has strong sinks in the ocean as well as the biosphere.

Secondly, sources other than those relevant within the Kyoto Protocol also need to be known, as they will also contribute to the observed concentration. Again, this is not a problem for the fluorinated gases (SF_6, PFC and HFCs) that only have anthropogenic emissions that are covered by the Kyoto Protocol. CH_4 and N_2O, however have significant natural sources that sometimes should not be considered in the Kyoto Protocol. Again, CO_2 stands out as the most complicated species, with strong oceanic and biospheric sources.

Finally, the transport in the atmosphere needs to be known. This involves winds on spatial and temporal scales from the global and hemispheric scale, transporting gases horizontally over long distances over days to months, down to the local scale where e.g. vertical transport in convection cells plays an important role over seconds to hours.

Estimates of emissions by the use of observations also set certain requirements for the measurements. Again, important issues are spatial and temporal resolutions. Simple analyses can be made with only a few measurement sites and only sampling that is sparse in time (e.g. weekly so called grab sampling which was common for many GHG in the 1970s and 1980s). However, more detailed analyses require a time resolution of only a few hours or better, to resolve the variations in wind systems bringing air masses towards the measurement stations. The spatial density of the observations is also important. This will restrict the spatial scale on which one can resolve the derived emissions, as will be discussed in the following.

D.2 Emissions on a global scale

The simplest approach one can take is the global one. In the model the atmosphere is then treated as a single box. This represents a strong simplification since transport effects are neglected. Neglecting transport means that uncertainties related to the transport do not influence the results, yielding results with smaller uncertainties. On the observation side, one would use globally averaged concentrations. The method is most suitable for components that are relatively well mixed in the atmosphere, which includes most Kyoto Protocol substances. The most problematic gas is probably CO_2, perhaps also some very short-lived HFCs. This approach can only be used to derive global total emissions. However, constraining global emissions can be useful in an evaluation of whether the emissions reported by the Parties are in agreement with the Kyoto Protocol on a global scale, i.e. it can be used to assess the effectiveness of the climate regime as a whole. As part of a system for verification of emissions, the global approach gives useful information about whether the total budget is correct, and can thus be used to determine whether further control of national inventories or improvement in the guidelines for reporting emissions is necessary.

We present one example of a study taking a global approach, applied to two fluorinated gases for which such an approach can best be used, namely HFC-134a (a CFC replacement gas) and SF_6 (Höhne and Harnisch, 2002). The results are depicted in Figure D.2 and Figure D.3. The shaded areas in the figures show the reported emissions from the main emitting countries, accumulated on top of each other. Only emissions from Annex I countries have been taken intro account. The lines represent global emissions based on atmospheric observations of concentrations and estimated loss, as calculated in a simple global box model. Whereas the loss for HFC-134a is large on the timescale of the 10 years studied (residence time 13.8 yr, yielding a loss of slightly above 50% in 10 yr) it is negligible for SF_6 (residence time 3200 yr, 0.3% loss over 10 yr).

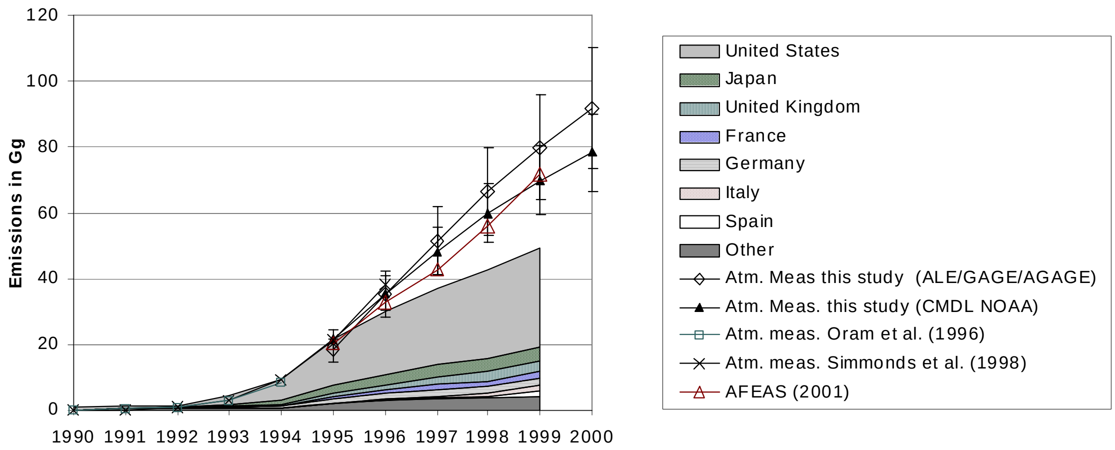


Figure D.2: Emission estimates of HFC-134a (Höhne and Harnisch, 2002).

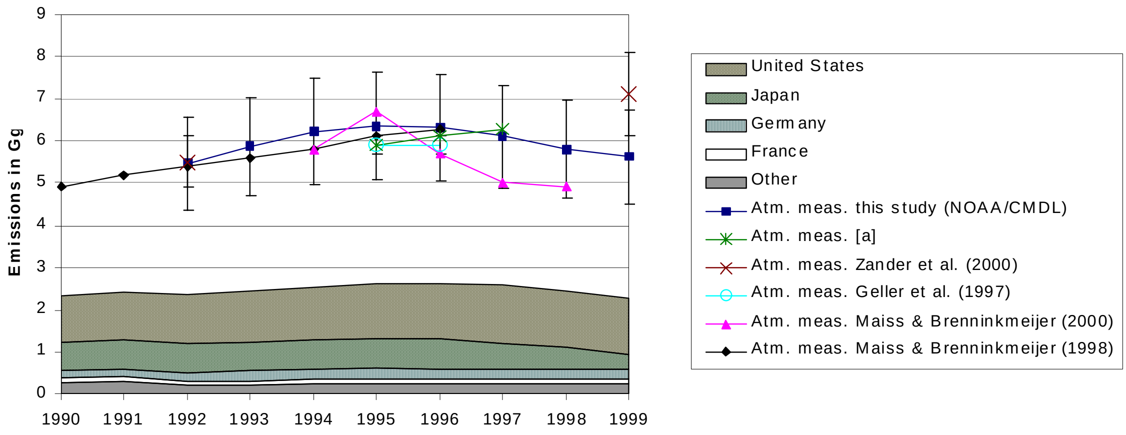


Figure D.3: Emission estimates of SF_6 as estimated by Höhne and Harnisch (2002) (see their paper for references to the various observations upon which the estimated have been based).

HFC-134a is an example of a compound in rapid growth. Its production started in 1980 and has increased rapidly since the early 1990s. Figure D.2 shows that the calculated emissions for HFC-134a are in good agreement with the reported emissions in the 1990-1995 period. After 1995 the emissions reported by the Annex I countries are significantly lower than those derived from the observations, possibly due to increasing emissions in the developing countries. There are uncertainties in the model estimates, reflecting mainly uncertainties in the observations. The model calculations have thus been performed with several observational datasets (see legend in Figure D.2 and references which can be found in Höhne and Harnisch, 2002).

For SF_6, shown in Figure D.3, the evolution of the reported and the indirectly derived emissions agree in that there was a slight increase in the beginning of the 1990s, followed by stabilization around the mid 1990s and thereafter a weak decline in the emissions. However there is a large deviation between the levels, as the reported emissions are only approximately half of the estimated ones. This could be due to emissions not yet reported from e.g. Russia or in China and other developing countries, although Höhne and Harnisch (2002) consider this as unlikely. This is thus an example of how the simple global approach can point to cases where there is a major gap in our knowledge.

D.3 Emissions on regional and country scales

Going from global to smaller scales can be done by adopting a range of approaches and models, with various degrees of sophistication. In any event, this introduces increasing uncertainties in the calculations. The results depend on our knowledge about natural sources and sinks, meteorological data to derive winds and on the accuracy of the model that is used, besides the accuracy of the measurements.

The use of dispersion models are showing promising results when applied to pollutants measured in extensive monitoring networks. When applied to Kyoto protocol substances, these would strongly benefit from an increased number of monitoring stations.

Inverse models are based on emission estimates. It is indicated that the uncertainties in natural sources and sinks must be greatly reduced to estimate anthropogenic emissions to the required accuracy when applied to Kyoto protocol substances.

D.3.1 Dispersion models

For the Kyoto Protocol substances only a very limited number of stations exist (four in Europe with sufficient temporal resolution measuring fluorinated Kyoto Protocol substances), as instrumentation and observation infrastructure have been expensive and designed mostly for the purpose of monitoring of global trends. There is probably a large potential in the use of dispersion model based methods for derivation of emissions of Kyoto Protocol substances by increasing the number of stations. An increasing number of stations will allow estimates of emissions at a decreasing spatial scale down to the level of individual countries in Europe. Three models (Stordal et al., 2004) have been used to infer emissions of halogenated source gases from high frequency observations from three European stations in a network developed in SOGE (System for Observation of halogenated Greenhouse gases in Europe). It has been found that European emissions of CFC-11, CFC-12, HCFC-141b and methyl chloroform have decreased substantially as a result of the Montreal protocol. For HFCs European emissions are increasing (HCF-152a) or stable (HFC-134a).

The results presented in this study are based on *in situ* high frequency real-time gas chromatographic measurements of a range of halogenated source gases measured in the SOGE project, which is operated as a network closely linked to the Advanced Global Atmospheric Gases Experiment (AGAGE) network, e.g. with a common calibration system. Data from three SOGE stations are used; Mace Head, Ireland, Jungfraujoch, Switzerland and Ny-Ålesund, Spitzbergen. Measurements have been made at Mace Head since 1994 within AGAGE. Since 2000 observations have been made at the three stations as part of the SOGE project.

Three different models have been used in estimation of emissions in this study:

The NAME model is a Lagrangian particle dispersion model (Manning et al., 2003). In the model abstract particles are moved around in the model domain according to three-dimensional meteorology fields from the complex numerical weather prediction model of the UK Meteorological Office. Each particle moves under the influence of the mean flow as well as wind meander and sub-grid turbulence, using a random walk technique. A simulated annealing technique is used to attribute elevated levels of the halogenated source gases back to their sources (Manning et al., 2004).

A trajectory approach has been taken in a second model (Reimann et al., 2004). Three-dimensional diabatic trajectories have been calculated using wind fields from Swiss Meteorological Institute MeteoSwiss up to July 2001, since then from the small scale alpine Local Model (aLMo). The model has been used in this study to identify potential emission source regions based on observations from the Jungfraujoch station, taking into account not only the position of the trajectories, but also the residence time of the trajectory spent over certain areas.

The 3D Chemistry Transport Model (CTM) Oslo CTM-2 (Grini et al., 2002) is being used also to constrain European emissions of halogenated source gases. The transport is driven by meteorological data from the European Centre for Medium-range Weather Forecasts (ECMWF). In this study we have used T42 and T21 horizontal resolutions. The transport scheme includes deep convection and boundary layer mixing.

Results

The halogenated source gases studied here have a background level which is unaffected by local or regional sources. In the calculations these values have been subtracted to allow studies of local and regional emissions.

Calculated concentrations of HCFC-141b from the Oslo CTM2, which has been run using bottom-up derived emissions, are compared to the observations at Mace Head in Figure D.4, showing a strong correlation between the two. The agreement between model results and observations are slightly better for the T42 than T21 resolution. The good correlation is a prerequisite for the model’s capability as a tool to estimate regional emissions.

The NAME model has been used to derive integrated European emissions. Figure D.5 shows the evolution of emissions from 1996 for several gases. The emissions have naturally been reduced strongly for CFC-11, CFC-12, HCFC-141b and methyl chloroform as a result of the Montreal protocol. For HFCs, which have been developed as substitutes, European emissions are increasing (HCF-152a) or stable (HFC-134a).

Distributions of emissions in Europe have been derived from the NAME model and the trajectory model. The distribution of emissions of HCFC-141b in Figure D.6 shows large emissions in particular in the Po Valley, but significant sources also elsewhere in continental Europe. The emissions were strongly reduced from 2000 to 2003, in line with the results in Figure D.5, still exhibiting a similar pattern.

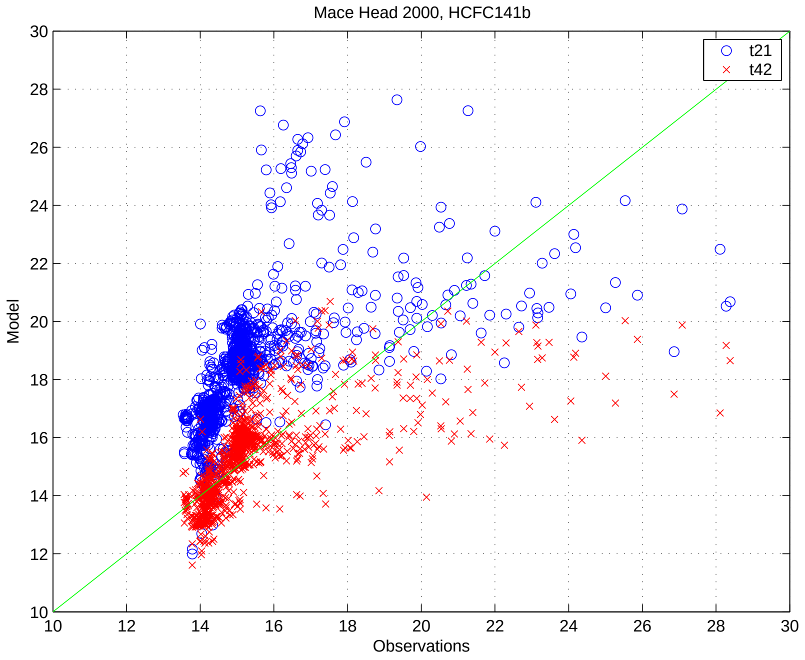


Figure D.4: Observed concentrations of HCFC-141b at Mace Head vs. model concentration from the Oslo CTM-2 model (T21 and T42 resolutions).

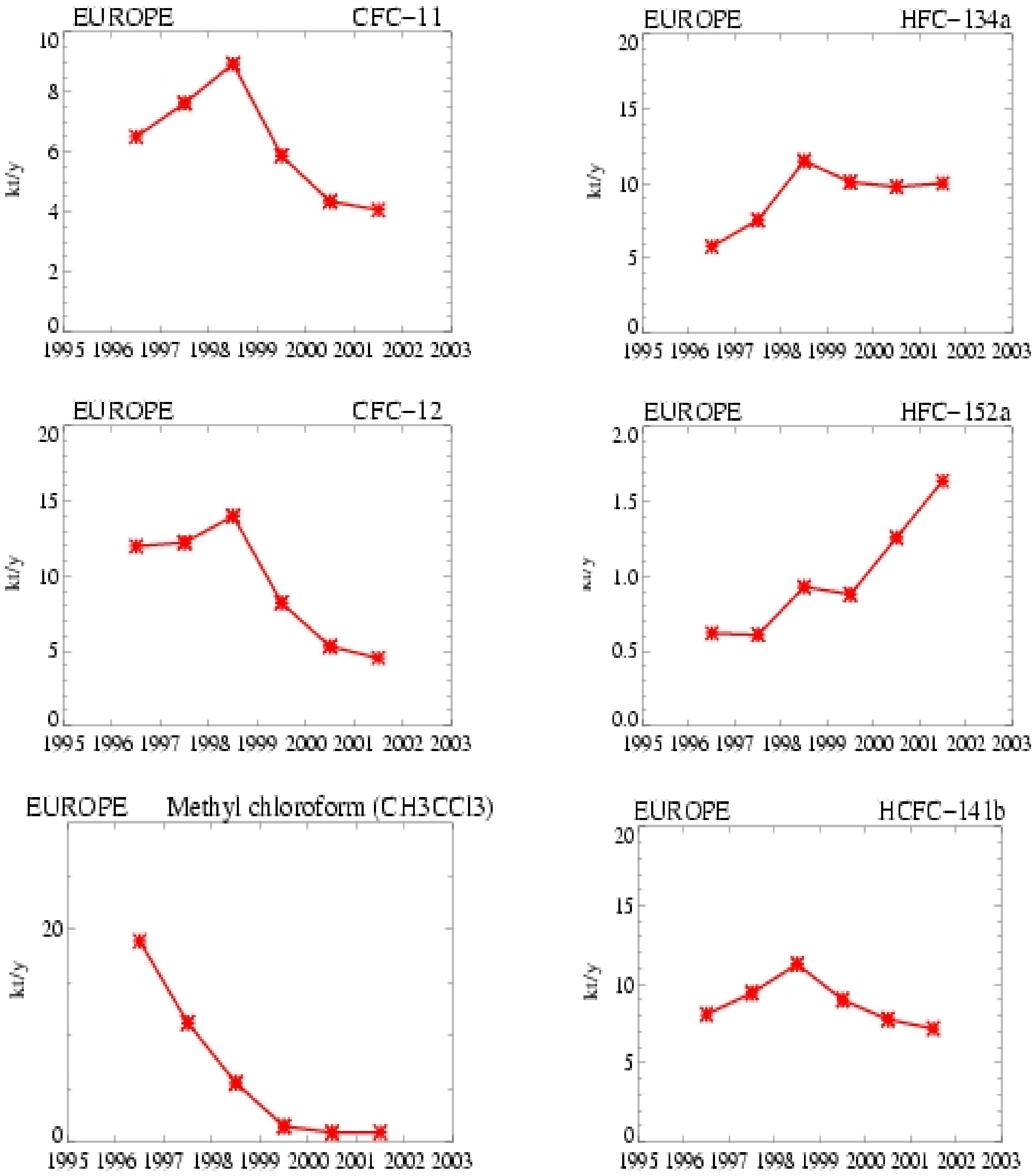


Figure D.5: Evolution of European emissions of selected halogenated source gases as estimated in the NAME model.

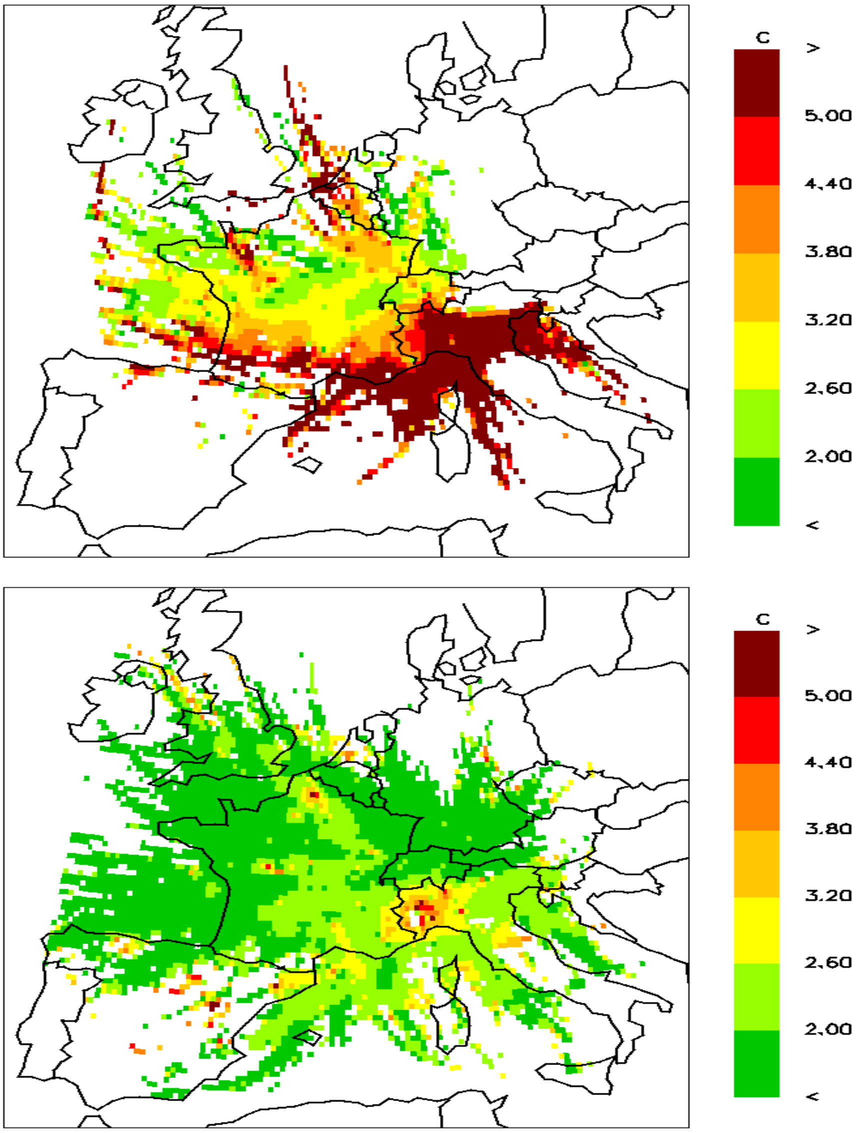


Figure D.6: Potential source regions for HCFC-141b resulting from trajectory modelling for year 2000 (upper) and 2003 (lower panel).

D.3.2 Inverse modelling

The methods described so far are based on modelling of GHG concentrations from given emissions and thereafter comparing the estimated concentrations with the measured concentrations. Alternatively, inverse models are set up to estimate emissions directly from the measured concentrations. As in most of the approaches above, one needs an atmospheric model describing all relevant atmospheric processes. Inverse models are computationally expensive and to some extent conceptually more complicated that the methods described previously in this section.

Inverse models have mainly been used to study emissions of CO_2 (e.g. Bousquet et al., 1999a; b; Kaminski et al., 1999a; b), but also CH_4 has been subject of study (e.g. Houweling et al., 1999). Inverse modelling of CO_2 has been successful in estimation of emissions on a continental scale, helping greatly in constraining the total budget of CO_2. Several models have been developed. Results from 8 different models were compared and interpreted in IPCC

(2001). In a more recent study, Gurney et al. (2002) reported emissions of sources and sinks for CO_2 in 22 different regions based on altogether 16 different models adopting two different inversion techniques. Although the results quite importantly improves the estimates of natural oceanic and terrestrial sources and sinks, they have not proven useful in constraining anthropogenic emissions. This is because the natural sources and sinks are much larger than the anthropogenic emissions, and because uncertainties are still large in the natural CO_2 budget components (see discussion in Kaminski and Heimann, 1999).

A huge reduction is needed in uncertainties of natural sources and sinks, a factor 20, in order for current inverse models to be able to estimate anthropogenic emissions to a degree of accuracy which will be needed to resolve the reductions in emissions required by the Kyoto Protocol (5.2% of the total GHG emissions from industrialised (Annex I) countries should be reduced from 1990 to 2008-12) (Gurney et al., 2002). Thus it is clear that for CO_2 there is a long way to go before inverse models can be of practical use in the emission work within the UNFCCC.

Appendix E

Background on the Montreal and Kyoto Protocol

This chapter is a shortened and somewhat changed version of Chapter 8 International Regulations on Halocarbons by P.M. Midgley and A. McCulloch in The Handbook of Environmental Chemistry 4E, Reactive Halogen Compounds in the Atmosphere editor P. Fabian.

CFC 11 and CFC 12 were introduced in the 1930s as replacements for toxic and flammable refrigerants. Production and emissions first remained low but increased rapidly in the 1960s with the spread of refrigeration in the developed world and as new uses, such as aerosol spray cans, were developed. By the early 1970s – CFC 11 and CFC 12 - had become ubiquitous trace constituents of the troposphere. Actually the **Association of Chemical Manufacturers** itself started a research programme to investigate possible effects of CFCs on the environment. The original aim was to assess the smog-forming potential but was soon altered when the later Nobel Price winners Molina and Rowland propounded their hypothesis of ozone depletion by CFCs in 1974.

The essence of the hypothesis was that, because of their exceptionally high chemical stability, CFCs would be totally stable in the troposphere and would diffuse unchanged to the stratosphere, where they would photolyse under the reaction of the sun's UV radiation to produce Cl atoms. In effect, chlorine atoms resulting from the photolysis of CFCs would increase the destruction of ozone that already was taking place by Cl atoms arising from naturally occurring chlorocarbons in the stratosphere. Owing to the cyclic nature of the reaction, each Cl atom could destroy many ozone molecules before it reacted with other species to form a stable and inactive molecule like HCl.

That was the basic hypothesis but, at that time, no ozone depletion had been observed and mathematical models of the atmosphere were incapable of describing all the processes consistently. Throughout the 1970s and early 1980s, the scientific community strove both to detect trends in stratospheric ozone, and improve the models.

In the meantime the releases of CFC 11 and CFC 12 continued to grow, as did releases of other compounds that could be transported to the stratosphere and decompose there to release chlorine or bromine: CFC 113, CFC 114, CFC 115, Halon 1211, Halon 1301, carbon tetrachloride and methyl chloroform all showed growth, although for many compounds this was not documented sufficient.

The growth in emissions was reflected in growth in atmospheric concentrations and was sufficiently alarming to set regulations in process, notwithstanding the inability of atmospheric models to agree or real ozone depletion to be detected.

In the mid 1970s, the widespread use of CFCs in aerosols was banned in USA. This resulted in an immediate reduction in emissions, but the long term trend of releases remained positive. Production was capped at the then current capacity in Europe, with a requirement to reduce the quantities used in aerosol propulsion by 30 %. This form of regulation – controlling total production and consumption, rather than each end use – was subsequently adopted in the Montreal Protocol and its revisions.

In 1981 there was still no evidence that the ozone layer was being affected, but – with the expectation that it could be depleted – the United Nations Environment Programme started a working group with legal and technical experts with the aim of securing a general treaty to tackle ozone depletion. This was finally agreed upon in **Vienna 1985** as the **Convention for**

the Protection of the Ozone layer, signed by 28 nations and subsequently ratified by 168. The nations agreed to take "appropriate measures ... to protect human health and environment against activities which are likely to modify the Ozone Layer – but the measures where unspecified. The main goal of the Convention was to encourage research, cooperation among countries and exchange of information.

The **Vienna Convention** set an important precedent: for the first time nations agreed in principle to tackle a global environmental problem before its effects were felt – or even scientifically proven. One fact that helped here was the fact that there are relatively few producers of ozone-depleting substances. This meant that those drafting the treaty could envisage controls on particular substances, rather than control on society's activities. In this respect, ozone-depleting substances are very different from greenhouse gases like carbon dioxide or methane, which are released as by products of societal activities, such as energy conversion and agriculture, rather than production and consumption.

E.1 The Montreal Protocol on substances that deplete the ozone layer

At the same time as the legal and technical experts were developing treaties, the scientific experts in the **C**oordinating **C**ommittee on the **O**zone **L**ayer (**CCOL** 1977) were reviewing results of atmospheric measurements and the models using them, and developing projects to extend understanding of ozone layer behaviour.

The first real evidence of ozone depletion came from Farman et al. who, in 1985, linked severe seasonal ozone depletion in the Antarctic to the growth in chlorine from CFCs in the Antarctic stratosphere. This paper was instrumental in promoting the **Montreal Protocol** , signed by 24 countries in 1987 and subsequently ratified by 165.

The Protocol, which came into force on 1st January 1989, is a flexible instrument; the provisions must be modified in the light of a virtually continuous scientific review process that reported to the Parties (Scientific Assessment of Ozone Depletion 1989, 1991, 1994, 1998, 2002). Reviews of the technologies available for providing substitutes for ODS (ozone depleting substances) occur with similar frequency together with reviews of the possible effects of ozone depletion.

The protocol also contains clauses to cover the special circumstances of several groups of countries, especially developing countries with low consumption rates that do not want the Protocol to hinder their development. As a result, regulations have evolved since 1989 as the scientifically driven requirements have changed and as the political and societal needs of countries have changed.

For the developed world the Protocol set out to control national production and consumption of CFCs (11, 12, 113, 114 and 115) and halons (1211, 1301,and 2402) as two distinct groups:

the CFCs were to be reduced by the year 1998 to 50% of their level in 1986, and production and consumption of halons were to be frozen at their 1986 levels in 1993. In both cases the different potency for ozone depletion of substances within each group was taken into account, using ODP (Ozone Depletion Potential) of each substance as a multiplier of the masses produced or consumed.

E.2 Amendments and Adjustments to the Protocol

E.2.1 London 1990

The CFCs controlled in the original version of the Protocol have lifetimes in the order of decades to several centuries. Consequently their atmospheric concentrations will be maintained by comparatively modest emissions. New calculations showed that a 77% reduction in emissions for CFC-11 and a 85% reduction in the emissions of CFC-12 would be required, simply to stabilise atmospheric concentrations on 1989 levels. Furthermore, the increases in concentration arising from production that were still allowed were not trivial – the CFC-12 levels could have been doubled by 2050 had the Protocol not been changed.

At the same time it became apparent that other compounds were capable of being transported into the ozone layer and augmenting ozone depletion by releasing chlorine there. Carbon tetrachloride (CCl_4), used principally as raw material for CFC-11 and CFC-12 production. The long atmospheric lifetime of 42 years made it an important ODS, even though the quantities released were smaller than CFC releases.

Methyl chloroform (CCl_3CH_3) has a much shorter lifetime (5 years) but because of larger releases its tropospheric concentration was higher than that of CCl_4. A significant part (over 10 %) could be expected to reach the stratosphere.

There were also releases of hydrochlorofluorocarbons (HCFCs) to consider. One of them HCFC-22 ($CHClF_2$), had been used as refrigerant in many years and in 1987 had a concentration of 100 ppt. There was concern that removing the option to use CFCs would result in a rapid and sustained increase in the use of HCFCs. Substitution in other than modest proportion could both increase the peak chlorine loading and sustain unprecedented levels of stratospheric chlorine.

Based on that, the Parties to the Montreal Protocol, meeting in London in 1990, agreed to phase out CFCs and halons by the year 2000; to extend the controls to any fully halogenated CFC (previously only named compounds were covered); to phase out Carbon tetrachloride by 2000 and Methyl chloroform by 2005. These controls extended to the developed world only.

E.2.2 Copenhagen 1992

HCFCs were included in a formula that set a "cap" on consumption and progressively reduced it to virtually zero by 2020, with complete phase-out in 2030. For each nation, the cap was set at the sum of its 1989 consumption of HCFCs plus 3.1 % of its total consumption of CFCs in that year. The calculations for the cap are based on ODP tonnes (that is the mass of each substance consumed multiplied by its ozone depletion potential).

In addition the Copenhagen amendments brought forward the dates for phase out of CFCs, CCl_4 and CCl_3CH_3 all to 1996 and halons to 1994. In part, this was in recognition of the far greater potency of bromine for ozone depletion than chlorine. For the same reason, CH_3Br (methyl bromide) was formally included in the protocol with a freeze on consumption in the developed world in 1995.

E.2.3 Vienna 1995

The first signs of the response of the environment to the Montreal Protocol could be discerned:

The increase in concentrations of CFC-11, 12, 113 and of Methyl chloroform had begun to slow down. However, the major review of ozone depletion in 1994 gave little ground for complacency, particularly because the extent and severity of Antarctic ozone holes continued to increase in 1992 and 1993. In 1995 CFCs, CCl_4 and CCl_3CH_3 and halons were all about to be phased out in the developed world, so that there was scope for change only as regards HCFCs and Methyl bromide. The cap percentage was reduced from 3.1 to 2.8 % and a phase out schedule for Methyl bromide was implemented. Both affected only the developed world.

E.2.4 Montreal 1997

There was a clearly discernible response of the halogen loading of the atmosphere to the reductions in production and consumption of halocarbons that actually had gone significantly faster than was required by the Protocol. Tropospheric chlorine loading peaked in 1993, from which it could be inferred that maximum stratospheric chlorine concentrations would occur a few years later. The peak in bromine loading could be expected to occur between 2000 and 2010. The Montreal amendments concentrated on consolidating the environmental improvements that had been made by the developed countries and extending the controls on HCFCs and Methyl bromide to the developing world. Summarised the controls for developing countries are: CFCs, CCl_4 and CCl_3CH_3,: freeze 1999 – phase out 2010 – Halons : freeze 2002 – phase out 2010 -HCFCs: freeze 2016 – phase out 2040 -Methyl bromide : freeze 2002 – phase out 2015. Between now and the phase out dates developing countries may continue to produce ODS at up to 15% of the rate in 1986. The quantity produced and the amount consumed is reported to UNEP. According to that the total production of CFCs in 1996 was less than 8% of the 1986 level.

E.2.5 Beijing 1999

The Beijing amendments include limits on the production of HCFCs in both developed (freeze in 2004) and developing countries (freeze in 2016). It also include stricter limits on the production of ODSs by developed countries for use in developing countries, as well as a global phaseout of a new species bromochloromethane (CH_2BrCl) in 2002

E.3 What might have happened without the Montreal Protocol?

In the free market that existed before 1974, CFCs showed remarkable growth. At that date, the combined production of CFCs was more than 800 000 t year^{-1} and had been growing at 10 % every year for over two decades. Had the ozone depletion theory not been evinced by Molina and Rowland in 1974 and had there not been a history of Antarctic ozone measurements dating back to 1956, that enabled the ozone hole to be identified as a recurrent phenomenon only a few years after the first spring in which significant depletion was observed, the first signs might have been severe, sudden changes to the ozone distribution in populated regions of the southern hemisphere.

Had the Antarctic ozone hole come as a surprise in the early 1990s with a global CFC ban in 2002 the ozone losses would have been more severe and have persisted well in the 22nd century. But as it looks now, stratospheric halogen will return by the early 2050 to the levels, which existed in the late 1970s, when the annual Antarctic ozone hole first became discernible.

E.4 Climate change and the Kyoto Protocol

This is arguably the next great environmental challenge to governments. The way that the threat of climate change from the accumulation of greenhouse gases has been addressed by international regulations bears some similarity to the negotiations of the Montreal Protocol and the scientific assessment of the two processes share a common heritage. The concept that atmospheric gases which absorb infrared radiation would affect the climate was already suggested in 1909 by S. Arrhenius.

However, many years elapsed before the proposition was subjected to detailed examination. Two WMO reports, one in 1981 “The stratosphere: Theory and measurements” and the second in 1985 “Atmospheric ozone: assessment of our understanding of the processes controlling its present distribution and changes” included the climatic implications of increasing concentrations of greenhouse gases into assessments made by the Coordinating Committee on the Ozone Layer for the Vienna Convention. These examined the physics of the atmospheric effects of increasing greenhouse gases and ozone depletion. But the first scientific reports that addressed all the implications, from the dynamics and possible detection of climate change through to its potential impacts on society were those of the Intergovernmental Panel on Climate Change in 1990. These reports provided the scientific bases for the negotiations that resulted in the **Rio Convention** in 1991. This has the ultimate objective of stabilisation of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. The **Rio Convention** bears the same relationship to climate change as the **Vienna Convention** to ozone depletion; similarly, the more rigorous controls are contained in Protocols to the Convention, the first of which is the **Kyoto Protocol**

In order for a gas to be implicated in climate change, it must both absorb infrared radiation and accumulate in the atmosphere. The first can be calculated relatively simply from its infrared absorption spectrum and a model of the natural transmittance of infrared radiation through the atmosphere. The second is a consequence of imbalance between the rate of addition of a compound to the atmosphere – the source flux – and its rate of removal – its atmospheric lifetime. Gases with long lifetimes like C_2F_6 (10 000 years) can accumulate in the atmosphere even if their fluxes are relatively small. At the other extreme, a gas that has a short lifetime can accumulate to relatively important concentrations, provided that its flux is large enough. This is the case for tropospheric ozone that has a lifetime of a few weeks at the earth’s surface, but accounts for 15 % of the calculated climate forcing, due to the very large “secondary” flux arising from atmospheric reactions of hydrocarbons and oxides of nitrogen.

The most important primary atmospheric greenhouse gas is carbon dioxide (CO_2), which accounts for 64 % of the increase in radiative forcing since pre-industrial times. Methane (CH_4) and nitrous oxide (N_2O), together, are calculated to contribute 28 % and halocarbons the remaining 6 %. The halocarbon contribution is expected to fall to 1.5 % by the year 2050. Carbon dioxide is, intrinsically, not a particularly powerful greenhouse gas but it has a very long environmental lifetime, so that the influence of an emission persists for many hundreds of years. Because of its position as the pre-eminent greenhouse gas, CO_2 is the reference compound against which the intrinsic effects of other greenhouse gases are judged, expressed as the ratio of the radiative forcing effect of a release of one kilogram of the target compound to the effect of a kilogram of CO_2. The problem that the effect of CO_2 changes with time has been addressed by integrating its radiative forcing effect, as well as that of other greenhouse gases, only up to a particular time horizon. The effect of this is to include progressively more of the effect of CO_2 as the time horizon lengthens, so that - as a general rule – GWPs decrease with longer time horizons. For most purposes, a time horizon of 100 years is used. Halocarbons are effective absorbers of infrared radiation, so their GWPs are in the range of several thousands. Consequently halocarbons in the form of hydrofluorocarbons and perfluorocarbons have been included in the Kyoto protocol as a part of the “basket” of greenhouse gases, emissions of which must be reduced. The other gases included are CO_2, CH_4, N_2O and sulphur hexafluoride (SF_6).

A significant commitment under the Rio Convention was the provision of inventories of national emissions of greenhouse gases. Secondary greenhouse gases, such as non-methane hydrocarbons and oxides of nitrogen, that can generate tropospheric ozone, are also included in the methodology of the emissions inventory. Using 1990 emissions as the baseline, the “aggregate anthropogenic carbon dioxide equivalent emissions” of the greenhouse gases described above must be reduced overall by at least 5% in the period 2008 to 2012. Carbon dioxide equivalence is actually the mass of the emissions multiplied by the 100 year Global Warming Potential of the gas concerned. The targets are, in fact, variable. The EU have targets within the Kyoto Protocol of 8 %, while the target for the USA is 7 % and some nations are allowed to increase releases of greenhouse gases - notably Australia, which is allowed an 8 % increase. In recognition of the fact that, in 1990, emissions of the halocarbon greenhouse gases not controlled by the Montreal Protocol were very small, 1995 is used as the base year for HFCs, PFCs and SF_6.

E.5 In conclusion

The Montreal Protocol is beginning to have the desired effect – although unambiguous detection of the beginning of the recovery of the ozone layer is expected to be well after the maximum loading of ozone depleting gases – still talking about time frames of decades. Although there is superficial similarity between the topics of ozone depletion and those of climate change, and indeed much scientific interaction between the two, climate change has much wider implications. The range of materials and activities to be considered in regulations and the range of consequences are far larger for climate change and, because of the very long lifetime of carbon dioxide, the timescale for recovery from any effect on climate is far longer. Nevertheless, the Kyoto Protocol is an important first step.

Norsk institutt for luftforskning (NILU)
Postboks 100, N-2027 Kjeller

REPORT SERIES SCIENTIFIC REPORT	REPORT NO. NILU OR 33/2005	ISBN 82-425-1677-4 ISSN 0807-7207	
DATE	SIGN.	NO. OF PAGES 76	PRICE NOK 150.-
TITLE Greenhouse gas monitoring at the Zeppelin station Annual report 2004		PROJECT LEADER Ove Hermansen NILU PROJECT NO. O-99093	
AUTHORS O. Hermansen, N. Schmidbauer, C. Lunder, F. Stordal, J. Schaug, C. Wehrli, I.T. Pedersen, K. Holmén, O.-A. Braathen (all NILU), J. Ström (Stockholm University)		CLASSIFICATION * A CONTRACT REF. Harold Leffertstra, SFT	

REPORT PREPARED FOR
Norwegian Pollution Control Authority (SFT)
P.O. Box 8100 Dep.
NO-0032 OSLO
NORWAY

KEYWORDS

Climate	Monitoring	Zeppelin station

ABSTRACT

The report summarises the activities and results of the greenhouse gas monitoring at the Zeppelin station situated on Svalbard in arctic Norway during year 2004.

The measurement programme is performed by the Norwegian Institute for Air Research (NILU) and funded by the Norwegian Pollution Control Authority (SFT).

NORWEGIAN TITLE

Klimagassovervåking ved Zeppelinstasjonen – Årsrapport 2004

ABSTRACT (in Norwegian)

Rapporten presenterer aktiviteter og måleresultater fra klimagassovervåkingen ved Zeppelinstasjonen på Svalbard i år 2004.

Måleprogrammet utføres av Norsk institutt for luftforskning (NILU) og er finansiert av Statens forurensningstilsyn (SFT).

** Classification: A Unclassified (can be ordered from NILU)*
B Restricted distribution
C Classified (not to be distributed)

Statlig program for forurensningsovervåking omfatter overvåking av forurensningsforholdene i luft og nedbør, skog, grunnvann, vassdrag, fjorder og havområder.

Overvåkingsprogrammet dekker langsiktige undersøkelser av:

- overgjødsling av ferskvann og kystområder
- forsuring (sur nedbør)
- ozon (ved bakken og i stratosfæren)
- klimagasser
- miljøgifter

Overvåkingsprogrammet skal gi informasjon om tilstanden og utviklingen av forurensningssituasjonen, og påvise eventuell uheldig utvikling på et tidlig tidspunkt. Programmet skal dekke myndighetenes informasjonsbehov om forurensningsforholdene, registrere virkningen av iverksatte tiltak for å redusere forurensningen, og danne grunnlag for vurdering av nye tiltak. SFT er ansvarlig for gjennomføringen av overvåkingsprogrammet.

Statens forurensningstilsyn
Postboks 8100 Dep, 0032 Oslo
Besøksadresse: Strømsveien 96

Telefon: 22 57 34 00
Telefaks: 22 67 67 06
E-post: postmottak@sft.no
Internett: www.sft.no
Bestilling: http://www.sft.no/skjema.html

Norsk institutt for luftforskning
Postboks 100, 2027 Kjeller
Besøksadresse: Instituttveien 18

Telefon: 63 89 80 00
Telefaks: 63 89 80 50
E-post: nilu@nilu.no
Internett: www.nilu.no