**Greenhouse gas monitoring at the Zeppelin station**
Annual report 2005

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# Greenhouse gas monitoring at the Zeppelin station

Annual report 2005

Report
993
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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), hydrofluoro-carbons (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 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 2005.

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# Summary

This annual report describes the activities and results in the project *Greenhouse gas monitoring at the Zeppelin station*, year 2005.

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 five 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.

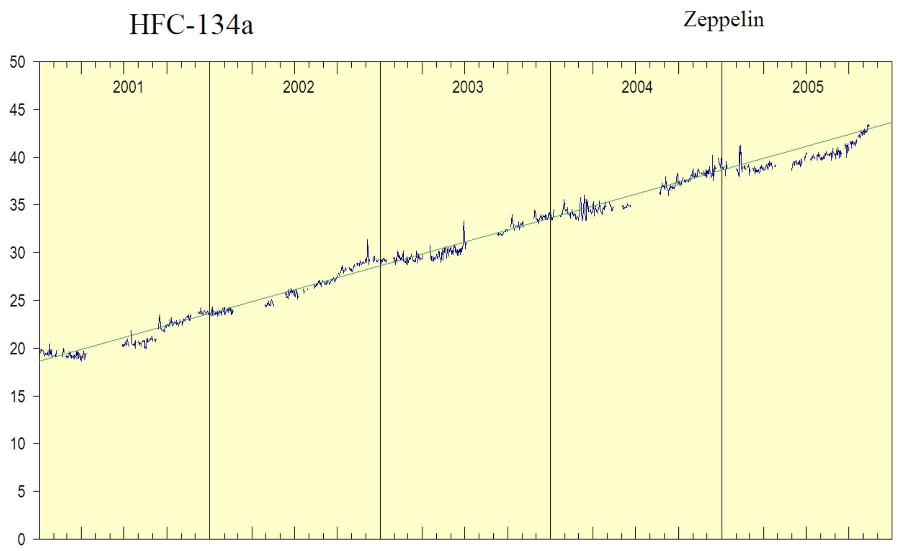


*Figure A: Measurements of HFC-134a at the Zeppelin station indicates a twofold increase in concentration levels over the past five years.*

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 continuously 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.e. perfluorocarbons and $N_2O$.

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 2001-2005. All concentrations in $ppt_v$, except for methane and carbon monoxide ($ppb_v$) and $CO_2$ ($ppm_v$). Trends are calculated from data for the period 2001-2005.*

| Compound | Formula | 2001 | 2002 | 2003 | 2004 | 2005 | Trend pr. year |
|---|---|---|---|---|---|---|---|
| **Methane** | $CH_4$ | 1820 | 1822 | 1826 | 1828 | 1825 | **+ 1.4** |
| **Carbon monoxide** | CO | | 129 | 138 | 134 | 124 | **- 1.8** |
| **Carbondioxide*** | $CO_2$ | 371 | 374 | 377 | 379 | 381 | **+ 2.8** |
| **Chlorofluorocarbons** | | | | | | | |
| CFC-11 | $CFCl_3$ | 263 | 264 | 263 | 260 | 260 | **- 1.7** |
| CFC-12 | $CF_2Cl_2$ | 551 | 560 | 564 | 563 | 559 | **+ 1.6** |
| CFC-113 | $CF_2ClCFCl_2$ | 82 | 83 | 82 | 81 | 81 | **- 0.4** |
| CFC-115 | $CF_3CF_2Cl$ | 8.3 | 8.5 | 8.6 | 8.6 | 8.6 | **+0.06** |
| **Hydrofluorocarbons** | | | | | | | |
| HFC-125 | $CHF_2CF_3$ | | 2.6 | | 3.7 | | |
| HFC-134a | $CH_2FCF_3$ | 21.7 | 26.1 | 31.0 | 36.0 | 40.8 | **+ 5.0** |
| HFC-152a | $CH_3CHF_2$ | 2.8 | 3.5 | 4.2 | 4.9 | 5.5 | **+ 0.7** |
| **Hydrochlorofluorocarbons** | | | | | | | |
| HCFC-22 | $CHF_2Cl$ | 161 | 172 | 179 | 183 | 188 | **+ 5.9** |
| HCFC-141b | $CH_3CFCl_2$ | 16.8 | 18.7 | 19.4 | 19.4 | 19.6 | **+ 0.5** |
| HCFC-142b | $CH_3CF_2Cl$ | 14.9 | 15.7 | 16.4 | 17.0 | 17.6 | **+ 0.7** |
| **Halons** | | | | | | | |
| H-1301 | $CF_3Br$ | 3.0 | 3.1 | 3.2 | 3.2 | 3.3 | **+0.08** |
| H-1211 | $CF_2ClBr$ | 4.4 | 4.5 | 4.6 | 4.7 | 4.6 | **+0.06** |
| **Halogenated compounds** | | | | | | | |
| Methylchloride | $CH_3Cl$ | 503 | 526 | 530 | 525 | 523 | **+ 1.7** |
| Methylbromide | $CH_3Br$ | 9.1 | 9.1 | 9.0 | 8.8 | 8.7 | **-0.14** |
| Methylendichloride | $CH_2Cl_2$ | 30.3 | 31.6 | 32.6 | 32.8 | 31.7 | **+ 0.5** |
| Chloroform | $CHCl_3$ | 11.2 | 11.1 | 11.1 | 11.1 | 11.1 | **-0.02** |
| Methylchloroform | $CH_3CCl_3$ | 36.5 | 33.1 | 28.4 | 23.3 | 19.1 | **- 4.7** |
| TriChloroethylene | $CHClCCl_2$ | 0.6 | 0.5 | 0.4 | 0.3 | 0.3 | **- 0.1** |
| Perchloroethylene | $CCl_2CCl_2$ | 4.5 | 4.0 | 3.7 | 3.4 | 2.8 | **- 0.4** |
| Sulphurhexafluoride | $SF_6$ | 5.0 | 5.1 | 5.3 | 5.5 | 5.8 | **+ 0.2** |

***** 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.

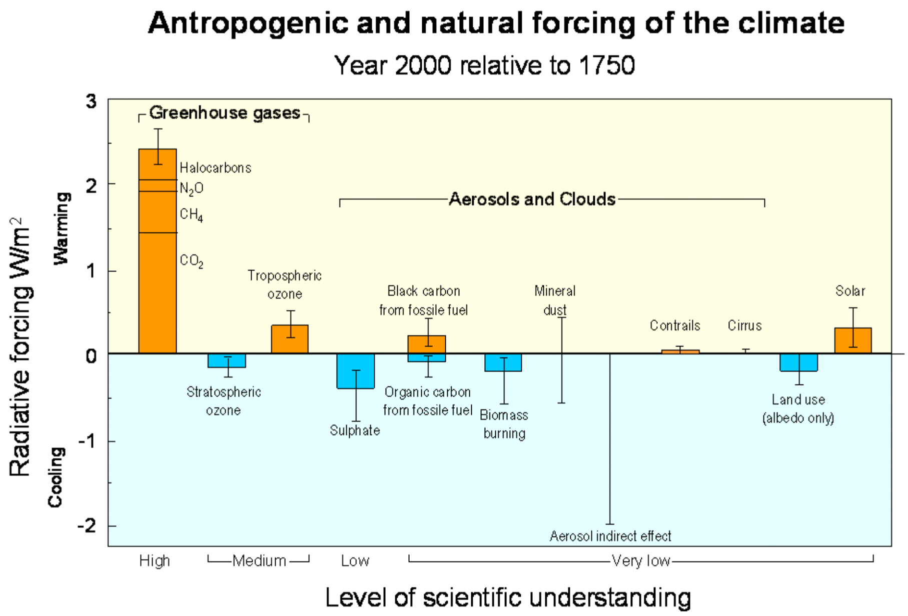


*Figure 1: Known factors and their influence on radiative forcing relative to pre industrial time. The vertical lines indicate the uncertainties for each factor. (Source: IPCC.)*

## 1.1 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.

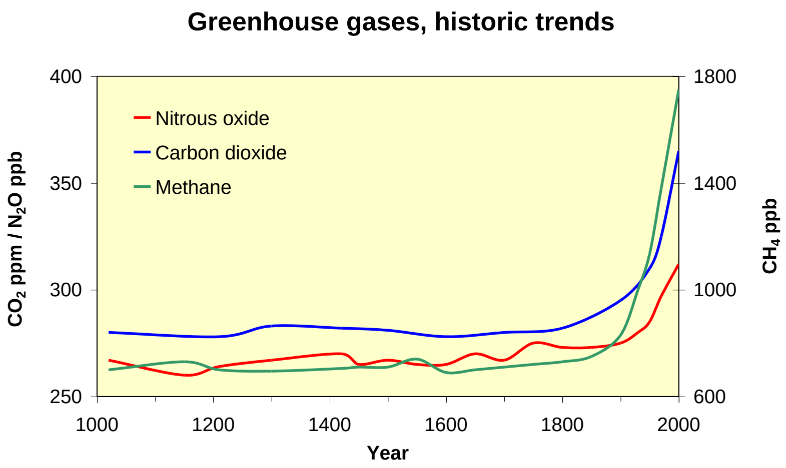


*Figure 2: Changes in concentration levels over time for some natural greenhouse gases.*

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.

## 1.2 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 20$^{th}$ 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 |
|---|---|---|---|---|---|---|
| **C**hloro**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 | |
| **H**ydro**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 |
| **H**ydro**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 |
| **P**er**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

## 1.3 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.

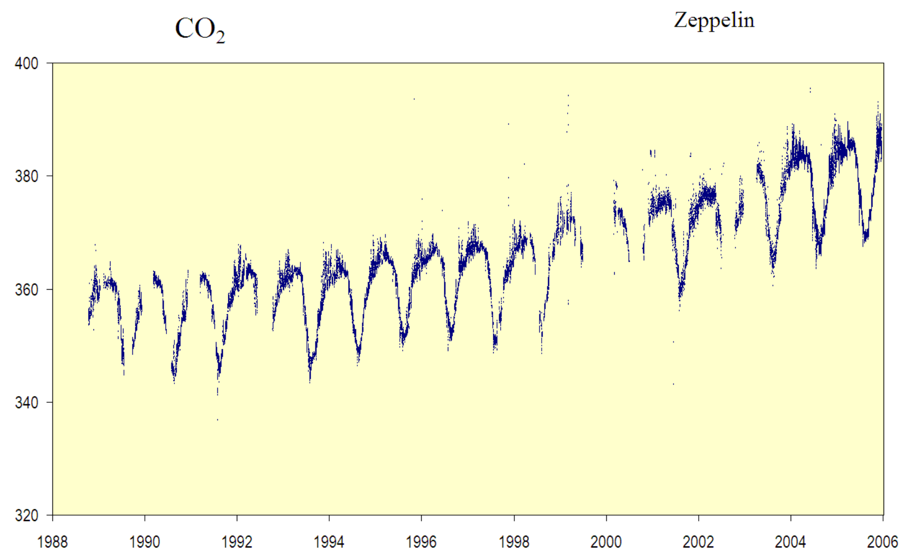


*Figure 4: SU have been monitoring $CO_2$ at Mt. Zeppelin since 1989.*

### 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.

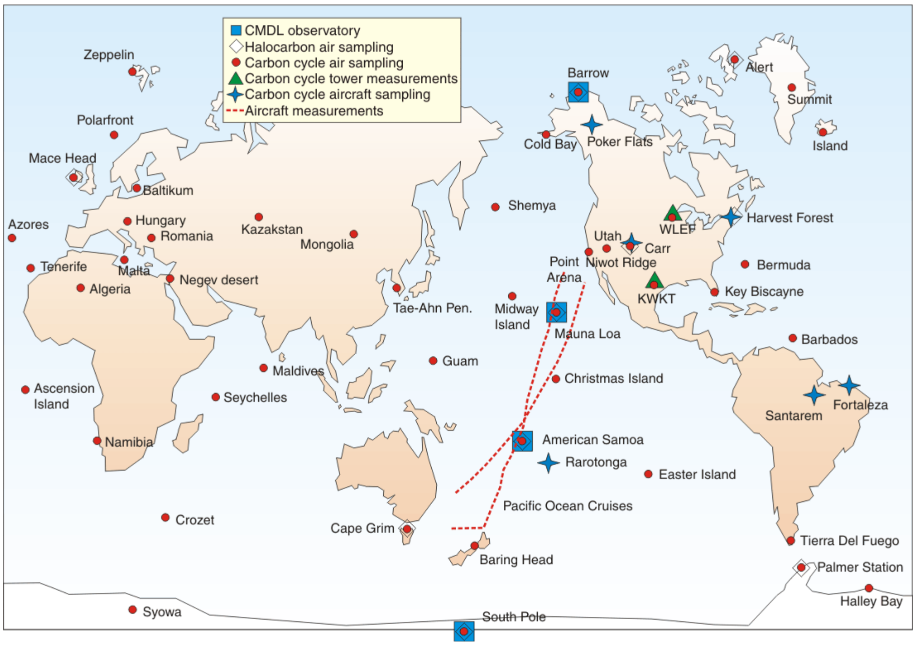


*Figure 5: NOAA's global air sampling network.*

## 2.3 Greenhouse Gas Monitoring Networks

### 2.3.1 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.

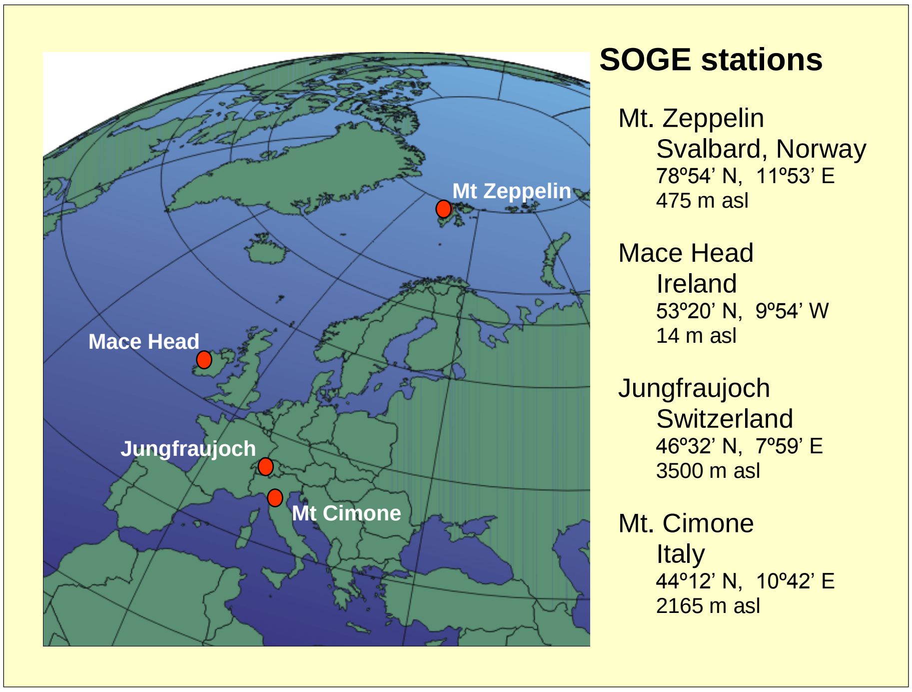


*Figure 6: The SOGE climate gas monitoring stations.*

### 2.3.2 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 behavior 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.

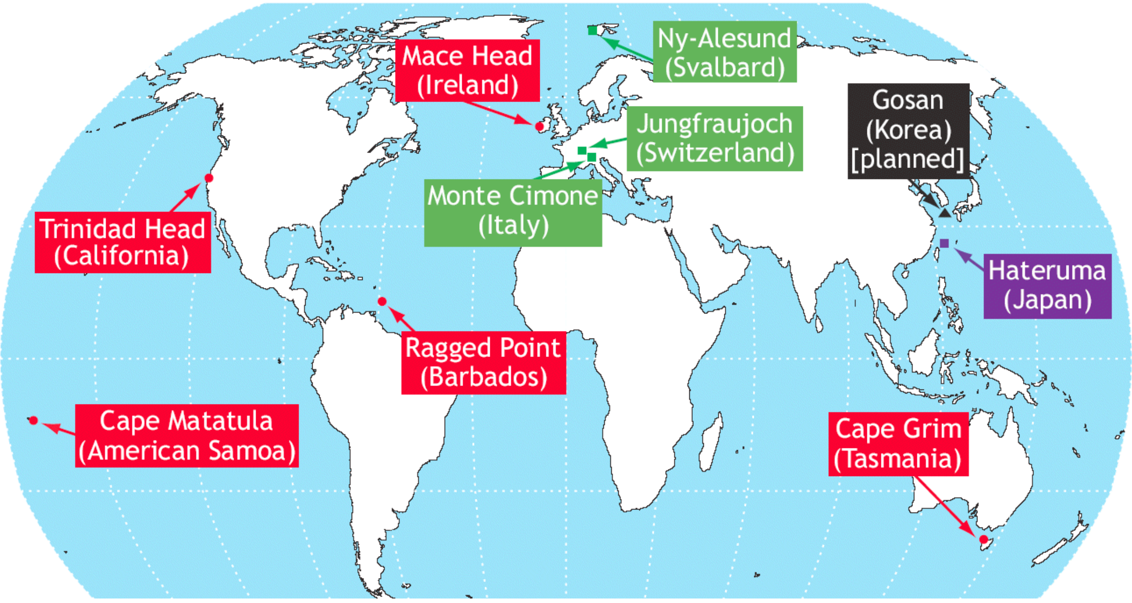


*Figure 7: The AGAGE network of monitoring stations.*

# 3 Instruments and methods

## 3.1 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 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. However, other stations in the networks are implementing new equipment enabling higher monitoring frequencies, higher precision and inclusion of new compounds. NILU will have to do the same in order to retain the status of the Zeppelin station as one of the most valuable sites for monitoring of background levels of trace gases.

Measurement results and trends based on the whole monitoring period 2001-2005 are shown in table A, appendix A.1.
Measurement results for the whole monitoring period 2001-2005 are shown as plots in appendix A.

## 3.2 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. Due to the time needed to rebuild at NILU and reinstall the instrument at the station, there are no data for the period January – April 2005.

The instrument is calibrated against new traceable standards with references to standards used under the AGAGE programme. Major audits were performed in September 2001 and July 2005 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 reports, concluding that methane measurements at the Zeppelin station can be considered to be traceable to the GAW reference standard.

## 3.3 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. Another major audit was performed July 2005. The results are published in EMPA-WCC reports, concluding that CO 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 August 2005, due to problems with a worn out sample pump. The overall data coverage is considered to be quite good for the year 2005.

## 3.4 Aerosol optical depth, Ny-Ålesund

### 3.4.1 Introduction

In recent years there has been an increased focus on climate change in the Arctic region. In particular, the extensive ACIA-report (ACIA, 2005) pointed to many challenging topics. Key findings are that the Arctic climate is warming rapidly and larger changes are projected. Further, the warming is faster than previously estimated and it will have global implications. Arctic vegetation zones are expected to shift, bringing wide-ranging impacts on animal, plants, and humans, as well as influencing the atmospheric composition. The reductions of sea ice will very likely increase marine transport and access to resources in the region with high potential to increase the local and regional pollution.

In the investigations of climate change, aerosols are of vital interest as they have a direct impact on the radiative balance by scattering of solar radiation and absorption of solar and thermal radiation. The dominating process depends on the absorption and scattering characteristics of aerosols defined by their composition, shape, and phase. In the Arctic knowledge about the optical properties of aerosols is of particular importance due to the special surface conditions in this region. Ice and snow give rise to very high albedos and water to very low albedo dominating the surface albedo in the region. Together with the albedo and clouds, aerosols are an important factor in controlling the UV radiation as well.

The lifetime of aerosols is short, in the order of days to weeks. At present local and regional anthropogenic sources are almost absent in Arctic region. Arctic haze commonly present in springtime is a well-known result of long-range transport into the region from mid-latitude sources in Russia, Europe and North America. In combination with transport there are favorable meteorological conditions with strong inversion in late winter and spring resulting in the high aerosol levels.

Recent studies indicate that boreal forest fires might be an important source of light absorbing aerosols containing black carbon (BC) in the Arctic region during summer (Stohl et al, 2006). In the Arctic, the importance of black carbon aerosols is even larger than elsewhere because atmospheric absorption is enhanced by the high surface albedo of snow and ice. Furthermore, the albedo of snow and ice can be reduced by the deposition of BC (Hansen and Nazarenko, 2004).

**Observations of aerosol optical properties in the European Arctic sector**

In a global perspective, satellites are becoming increasingly important for measuring total columns and vertical profiles of aerosols (E.g. MODIS, MISR, CALIPSO). However, satellite measurements of aerosol properties in Polar Regions are very difficult due to the special conditions with high surface albedo, large solar zenith angle, long path through the atmosphere, and low background aerosol concentrations. Consequently ground-based networks are of particular importance in these regions.

Aerosols optical properties are measured at a large number of ground-based sites around the world. AERONET[1] (Aerosol Robotic Network, Holben et al., 1998) aims at the assessment of aerosol properties and the validation of satellite retrieval of aerosols optical properties. The network compiles data around the globe, including about 60 European sites but only one station, Hornsund, (77 $^o$N, 15$^o$E), in the European Arctic.

The World Meteorological Organization, Global Atmospheric Watch (WMO GAW) programme runs a small trial network of 13 background stations operating sun-phtometers (Precision-filter-radiometer, PFR) around the world (see Wherli, 2005). Six sites are or will be operated in Europe. Data are available through a web-site[2]. Two sites are located in the Arctic sector, the site in Ny-Ålesund and one in Sodankylä in Northern Finland.

This chapter presents optical properties of aerosols measurements from the Sverdrup station in Ny-Ålesund particularly aerosol optical depth (AOD) measurements in 2005. The measurements are discussed in relation to observations of chemical constituents and transport into the region and compared to the AOD measurements in the period 2002-2005.

### 3.4.2 Location and experimental details 2005

The PFR measurements in Ny-Ålesund are part of the global network of aerosol optical depth (AOD) observations, which started in 1999 on behalf of the WMO GAW program. The instrument is located on the roof of the Sverdrup station, Ny-Ålesund, close to the EMEP station on the Zeppelin Mountain (78.9°N, 11.9°E). The PFR has been in operation since May

[1] http://aeronet.gsfc.nasa.gov
[2] http://wdca.jrc.it/

2002. In Ny-Ålesund the polar night lasts from 26th October to 16th February, leading to short observational seasons. However during the summer it is possible to measure day and night if the weather conditions are satisfactory. The instrument measures direct solar radiation in four narrow spectral bands centred at 862, 501, 411, and 368 nm. Data quality control includes instrumental control like detector temperature and solar pointing control as well as objective cloud screening. The signals are recorded every 1.25 seconds and are given as one minute averages. In the calculations of the AOD values it is necessary to correct for the absorption of UV by ozone. For this, we have used daily ozone values from TOMS[3] in the calculations. AOD measurements were obtained only on 38% of the possible days in 2005 due to bad weather conditions. The number of days where measurements can be performed is reduced due to foggy weather conditions, as the measurements are dependant on direct solar radiation. Moving the instrument to the EMEP station on the Zeppelin Mountain can increase the number of observations during clear sky conditions as this station is often located above the fog. Further there are less shades from surrounding mountains on this high station. However, so far a necessary sun tracker is not available.

### 3.4.3 AOD measurements in 2005 at Ny-Ålesund

Hourly AOD values measured in Ny-Ålesund by the PFR-instrument are presented in Figure for three different wavelengths. The observations show increased aerosol levels during the Arctic haze period in the spring. However, there are also short episodes later in the year with elevated levels of AOD. These episodes are discussed in section 3.4.4.

[3] http://toms.gsfc.nasa.gov/ozone/ozone.html

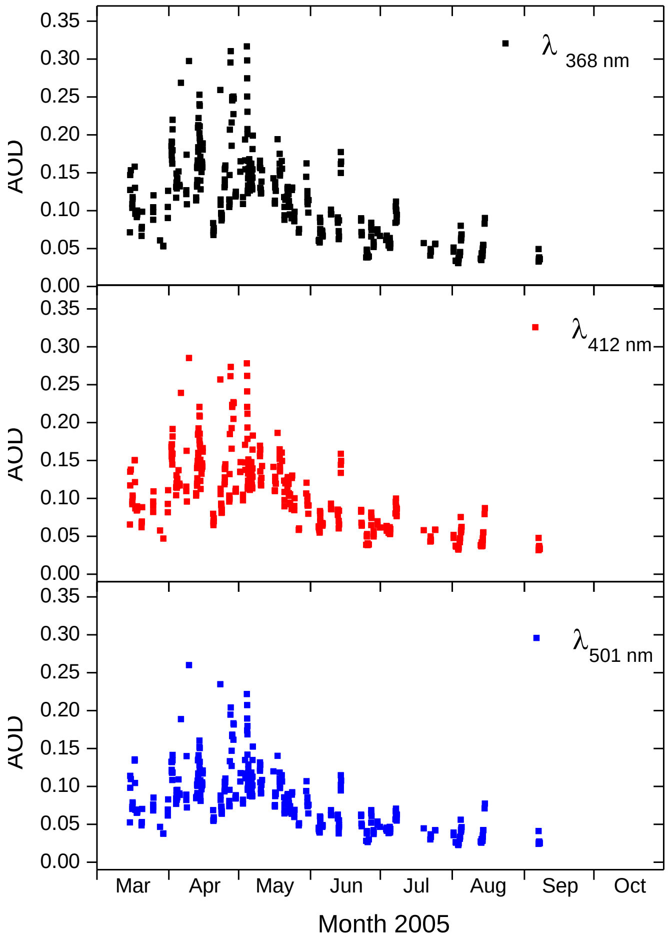


*Figure 8: Hourly AOD values measured in Ny-Ålesund during 2005*

The annual daily mean AOD in 2005 at $\lambda = 501$ nm is 0.08 ($\sigma = 0.035$) based on measurements on 70 days. Mean AOD during Arctic haze (March-May) was 0.10 ($\sigma = 0.029$) and during summer the mean value was 0.04 ($\sigma = 0.016$). The maximum value in 2005 at 501 nm was 0.26 at 9 April.

The Ångstrom exponent, $\alpha$, provides information about the size of the aerosols. Larger values of $\alpha$ imply a relatively high ratio of small particles. In general aerosols transported over a wider area is small compared to primary local source aerosols as sea salt. According to Smirnov et al. (2003) the representative threshold value for maritime aerosol types are Ångstrøm exponents below 1.0. Aerosols from combustion processes and aerosols produced in the atmosphere by secondary processes tend to be small and might be transported over large regions.

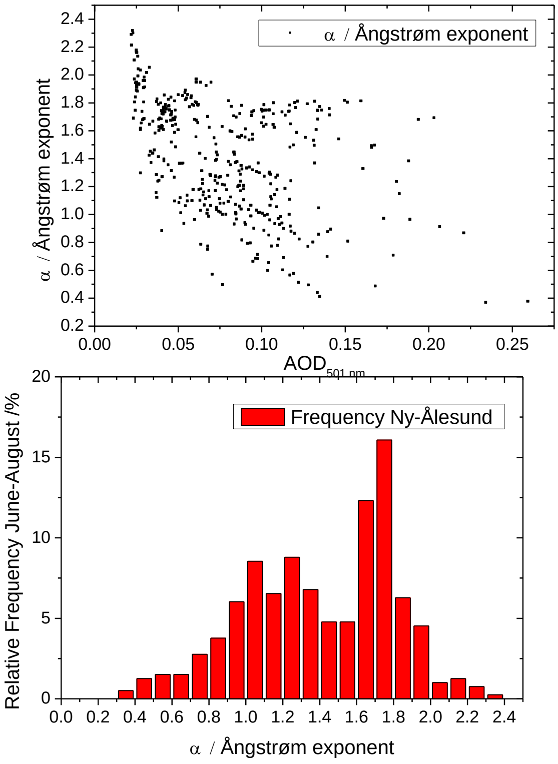


*Figure 9: Lower panel: The relative frequency of hourly averaged Ångstrøm exponents, α, during 2005. Upper panel: α based on hourly averaged data from Ny-Ålesund during 2005.*

Figure shows the Ångstrøm exponents and how it relates to the measured AOD values at 501 nm. The results must be interpreted with caution, as they represent few days with measurements. The upper panel in the Figure demonstrates that there is a tendency that low AOD values are connected with high Ångstrøm exponents and higher AOD values are connected with low Ångstrøm exponents. This suggests that episodes with high AOD values are connected with larger aerosols. The explanation to this needs further evaluation but the lowest α values may be due to thin cirrus clouds, because of the difficulty of the automatic cloud-screening algorithm to detect them.

In the lower panel of Figure hourly relative frequencies of the Ångstrøm exponents, α, during 2005 are displayed. The α values are widely distributed with signs of two peaks centred at α = 1.70 and α = 1.20. 30% of the α is in the range from 1.65 - 1.75, but as much as 25 % in range from 1.05 - 1.25 as well. Only 21 % of the Ångstrøm exponents are below 1.0 in Ny-Ålesund the typical value for maritime aerosols.

The high α values imply large loading of fine aerosols. The observed α values are not trivial to explain, and further studies and observations are necessary to confirm the origin of these fine particles.

### 3.4.4 Discussion of episodes with elevated AOD observations in 2005 at Ny-Ålesund

Figure displays the AOD values at λ = 501 nm together with the Ångstrøm exponents and daily filter analysis of particulate $SO_4^{2-}$, $NO_3^-$, and $Cl^-$ from the Zeppelin observatory.

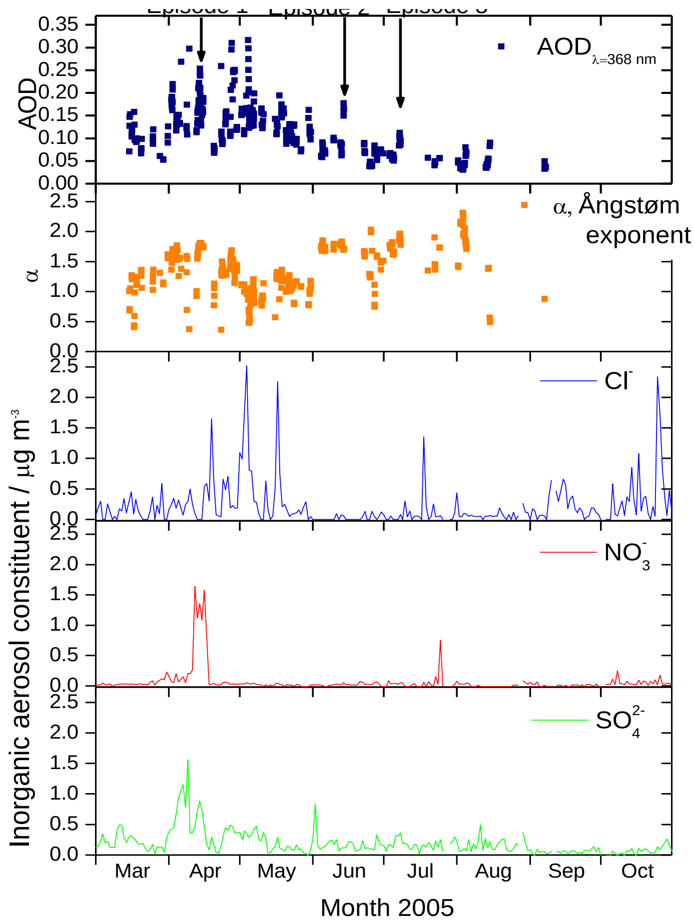


*Figure 10: AOD measurements from Ny-Ålesund in 2005 together with Ångstrøm exponents and inorganic aerosols constituents from the Zeppelin observatory.*

Three different episodes, 1-3, are indicated at the top of the Figure and the Figure displays that the episodes with elevated AOD do not necessarily coincide with increased levels of inorganic aerosol constituents measured at the Zeppelin station. Table  summarises the characteristics of the episodes.

*Table 2: Characteristics of selected episodes in Ny-Ålesund 2005*

| | Date | Max. $AOD_{\lambda=501\ nm}$ | Ångstrom exponent, α mean values | Inorganic constituents |
|---|---|---|---|---|
| Arctic haze | March - April | 0.25 (average 0.12) | 1.18 $\sigma =$ 0.27 | Medium |
| Episode 1 | 13 -14 April | 0.16 | 1.73 $\sigma =$ 0.08 | High |
| Episode 2 | 12 - 14 June | 0.11 | 1.77 $\sigma =$ 0.06 | Low |
| Episode 3 | 7 - 8 July | 0.08 | 1.88 $\sigma =$ 0.06 | Low |

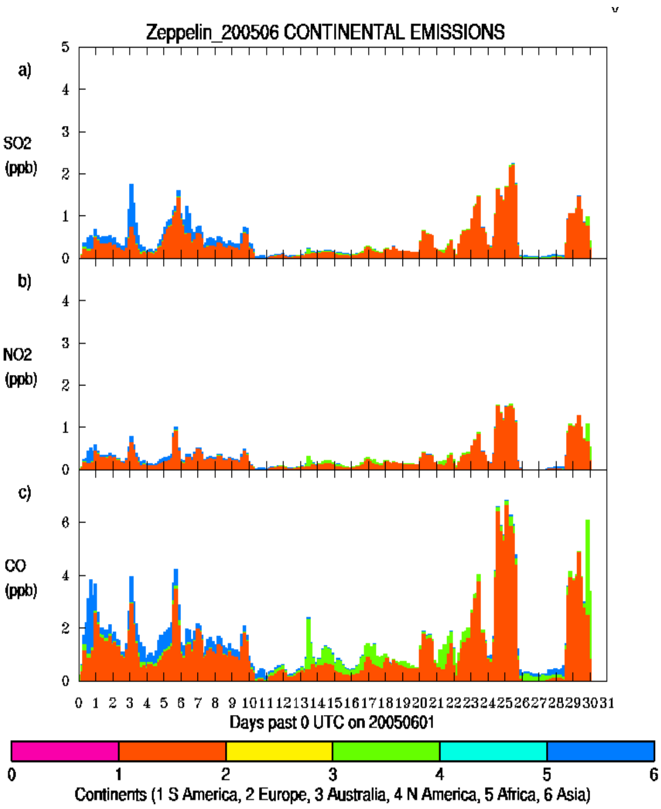


*Figure 11: The continental emissions influencing the air masses arriving daily at Zeppelin in June 2005 (Episode 2).*

The Ångstrøm exponents, α, were relatively high during the episodes indicating small aerosols typical for long-range transport. During *episode 2 and 3* very low concentrations of inorganic aerosols constituents were detected at the Zeppelin observatory. To interpret the episodes and the influence of transport on measurements taken at the EMEP station at the Zeppelin Mountain we have performed backward simulations with the Lagrangiain particle dispersion model FLEXPART (Stohl et al., 2005). The model results and a description of the simulations are available at the web page http://zardoz.nilu.no/~andreas/STATIONS/ZEPPELIN/index.html.

Figure shows the anthropogenic emission contribution for $SO_2$, $NO_2$ and CO from the different continents in ppb arriving at Zeppelin in June 2005. $SO_2$ and $NO_2$ are tracers for inorganic aerosol constituents while CO is a good tracer for absorbing aerosols containing BC. The simulation shows that during *episode 2*, 12$^{th}$ – 14$^{th}$ June, there were almost no transport of $SO_2$ and $NO_2$ to Zeppelin. This is consistent with the low values of inorganic compounds measured at the same time. However, at the same time there was a contribution of CO mainly from North America, suggesting that the elevated AOD measurements are due to North American anthropogenic emissions. The most prominent source is biomass burning. Similar analysis of the *episode 1* during the Arctic haze period, 13$^{th}$ – 14$^{th}$ April (see web page), indicates that the dominating anthropogenic source for both inorganic compounds and CO was in Europe and that there was a small contribution from Asia. For *episode 3*, 7$^{th}$ – 8$^{th}$ July (see web page), the main source of all compounds considered here seemed to be Europe with an additional small contribution of CO from North America.

### 3.4.5 AOD measurements 2002-2005

Figure presents the AOD measurements at 501 nm in Ny-Ålesund for the years 2002 - 2005. As expected the AOD values are considerable higher during the Arctic haze period for all years. Yet, Figure illustrates that there are several episodes during the years with short-term elevated AOD values in the summer and autumn as

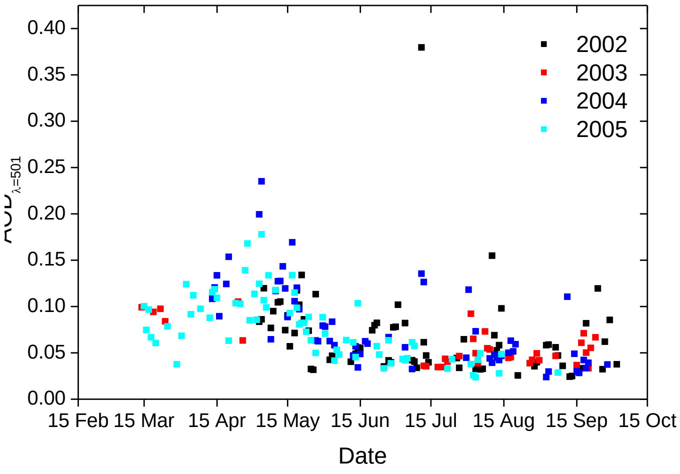


*Figure 12: Daily average aerosol optical depth (AOD) measured in Ny-Ålesund during 2002-2005.*

well. Analyses of such episodes are important to understand the effect of pollution transported into the region. Stohl and co-workers (Stohl *et al.* 2006) analysed the observed episode in the end of July 2004. They showed that huge emissions from boreal forest fires in North America, with light absorbing aerosol containing BC, was transported into the region and very likely explain the elevated AOD levels.

The time series of four years is much too short for trend analysis. However, we have calculated seasonal and annual mean AOD values to compare the years and the seasonal variations. Annual mean values, mean values for the Arctic haze and the summer months based on daily means are presented in Table The results show clear seasonal variations and only minor variations from year to year.

*Table 3: Annual mean values and mean values for the period March - May and June – August 2005. The numbers in parenthesis gives the number of days with measurements.*

| Year | Mean March-May (No. of days) | Mean June-Aug (No. of days) | Annual mean (No. of days) | Max daily mean (Date) |
|---|---|---|---|---|
| 2002 | 0.09 (19) σ = 0.027 | 0.06 (30) σ = 0.058 | 0.07 (72) σ = 0.047 | 0.38 (11 July) |
| 2003 | 0.09 (7) σ = 0.015 | 0.04 (20) σ = 0.014 | 0.06 (35) σ = 0.021 | 0.10 (14 March) |
| 2004 | 0.12 (23) σ = 0.042 | 0.06 (27) σ = 0.026 | 0.08 (60) σ = 0.045 | 0.24 (4 May) |
| 2005 | 0.10 (43) σ = 0.029 | 0.04 (26) σ = 0.016 | 0.08 (70) σ = 0.035 | 0.18 (5 May) |

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URL: http://www.wmo.ch/pages/program/arep/gaw/documents/gaw162.pdf

# Appendix A

# Measurement results

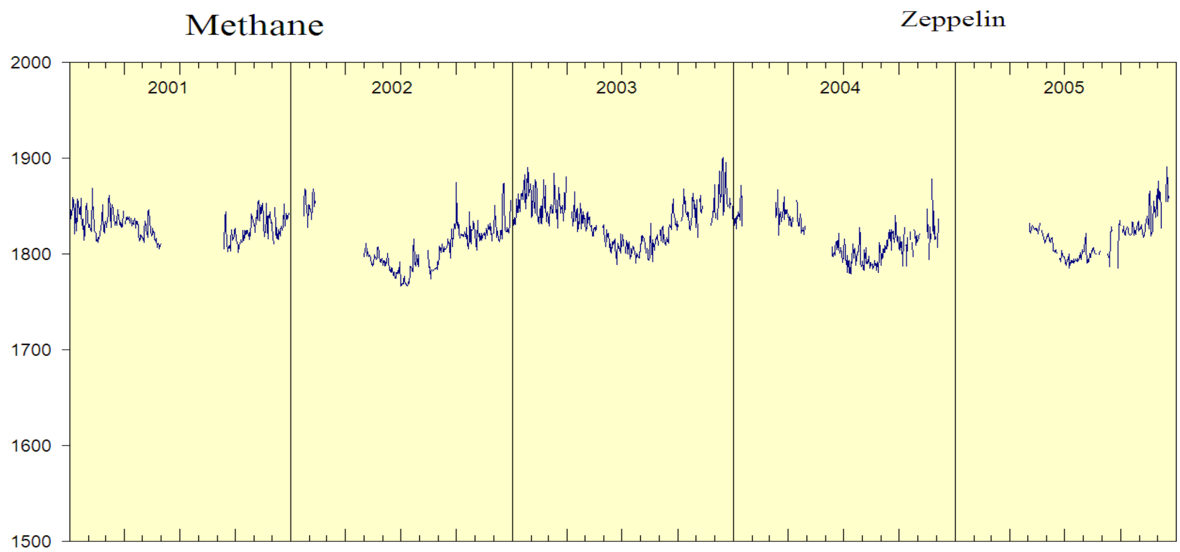
# A.1 Greenhouse gases, levels and trends

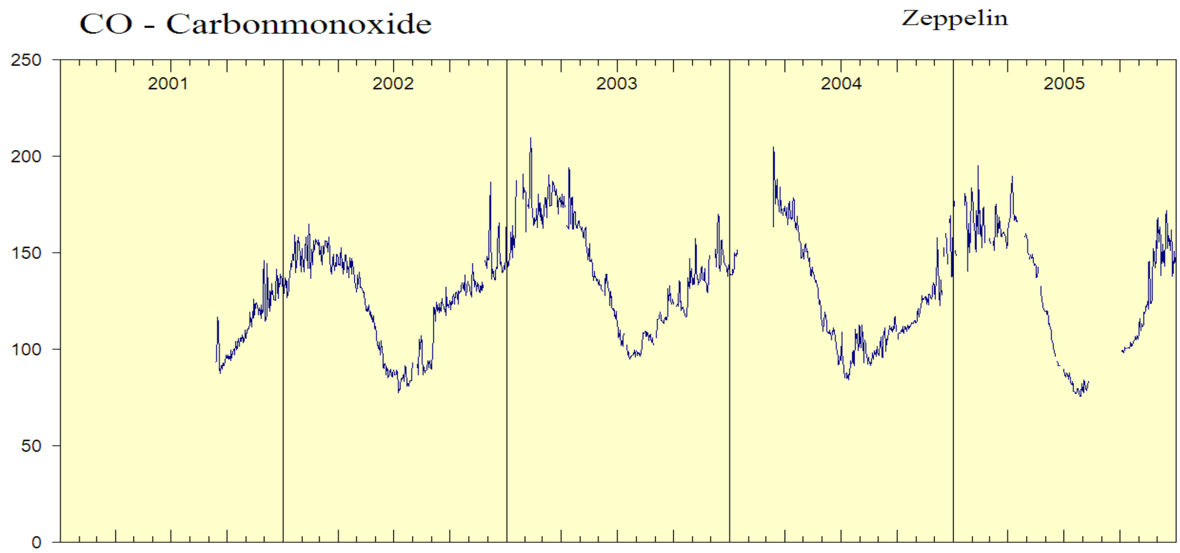
*Table A: Monthly and yearly average concentration levels of greenhouse gases at the Zeppelin station year 2001-2005. All concentrations in $ppt_v$, except for methane and carbon monoxide ($ppb_v$) and $CO_2$ ($ppm_v$). Trends are calculated from data for the period 2001-2005.*

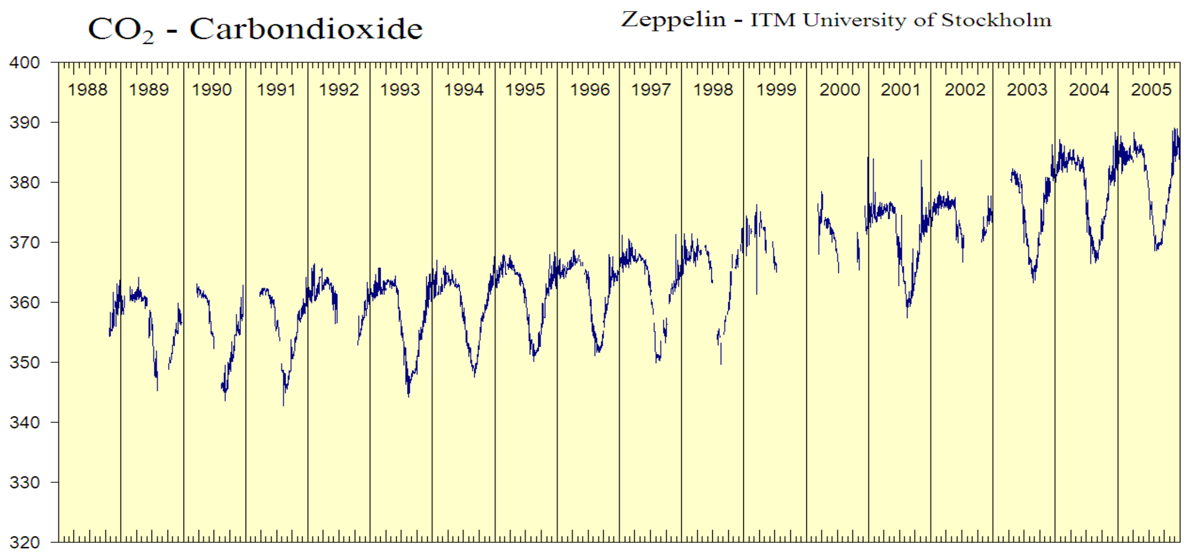
| Compound | Formula | 2001 | 2002 | 2003 | 2004 | 2005 | Trend pr. year |
|---|---|---|---|---|---|---|---|
| **Methane** | $CH_4$ | 1820 | 1822 | 1826 | 1828 | 1825 | **+ 1.4** |
| **Carbon monoxide** | CO | | 129 | 138 | 134 | 124 | **- 1.8** |
| **Carbondioxide*** | $CO_2$ | 371 | 374 | 377 | 379 | 381 | **+ 2.8** |
| **Chlorofluorocarbons** | | | | | | | |
| CFC-11 | $CFCl_3$ | 263 | 264 | 263 | 260 | 260 | **- 1.7** |
| CFC-12 | $CF_2Cl_2$ | 551 | 560 | 564 | 563 | 559 | **+ 1.6** |
| CFC-113 | $CF_2ClCFCl_2$ | 82 | 83 | 82 | 81 | 81 | **- 0.4** |
| CFC-115 | $CF_3CF_2Cl$ | 8.3 | 8.5 | 8.6 | 8.6 | 8.6 | **+0.06** |
| **Hydrofluorocarbons** | | | | | | | |
| HFC-125 | $CHF_2CF_3$ | | 2.6 | | 3.7 | | |
| HFC-134a | $CH_2FCF_3$ | 21.7 | 26.1 | 31.0 | 36.0 | 40.8 | **+ 5.0** |
| HFC-152a | $CH_3CHF_2$ | 2.8 | 3.5 | 4.2 | 4.9 | 5.5 | **+ 0.7** |
| **Hydrochlorofluorocarbons** | | | | | | | |
| HCFC-22 | $CHF_2Cl$ | 161 | 172 | 179 | 183 | 188 | **+ 5.9** |
| HCFC-141b | $CH_3CFCl_2$ | 16.8 | 18.7 | 19.4 | 19.4 | 19.6 | **+ 0.5** |
| HCFC-142b | $CH_3CF_2Cl$ | 14.9 | 15.7 | 16.4 | 17.0 | 17.6 | **+ 0.7** |
| **Halons** | | | | | | | |
| H-1301 | $CF_3Br$ | 3.0 | 3.1 | 3.2 | 3.2 | 3.3 | **+0.08** |
| H-1211 | $CF_2ClBr$ | 4.4 | 4.5 | 4.6 | 4.7 | 4.6 | **+0.06** |
| **Halogenated compounds** | | | | | | | |
| Methylchloride | $CH_3Cl$ | 503 | 526 | 530 | 525 | 523 | **+ 1.7** |
| Methylbromide | $CH_3Br$ | 9.1 | 9.1 | 9.0 | 8.8 | 8.7 | **-0.14** |
| Methylendichloride | $CH_2Cl_2$ | 30.3 | 31.6 | 32.6 | 32.8 | 31.7 | **+ 0.5** |
| Chloroform | $CHCl_3$ | 11.2 | 11.1 | 11.1 | 11.1 | 11.1 | **-0.02** |
| Methylchloroform | $CH_3CCl_3$ | 36.5 | 33.1 | 28.4 | 23.3 | 19.1 | **- 4.7** |
| TriChloroethylene | $CHClCCl_2$ | 0.6 | 0.5 | 0.4 | 0.3 | 0.3 | **- 0.1** |
| Perchloroethylene | $CCl_2CCl_2$ | 4.5 | 4.0 | 3.7 | 3.4 | 2.8 | **- 0.4** |
| Sulphurhexafluoride | $SF_6$ | 5.0 | 5.1 | 5.3 | 5.5 | 5.8 | **+ 0.2** |

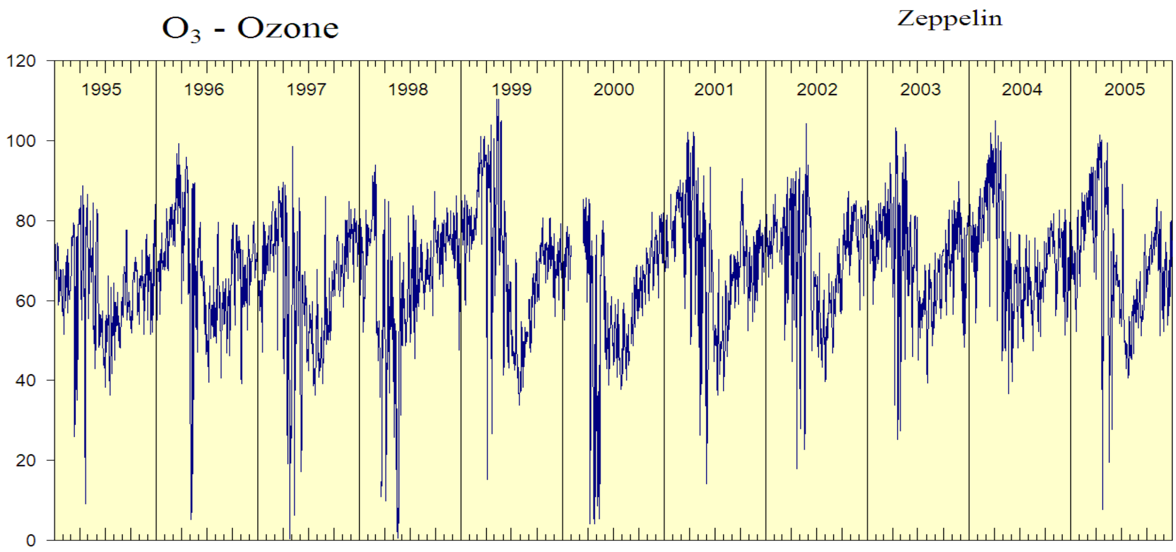
* Measurements of Carbondioxide performed by ITM, Stockholm University

## A.2 Non-halogenated greenhouse gases

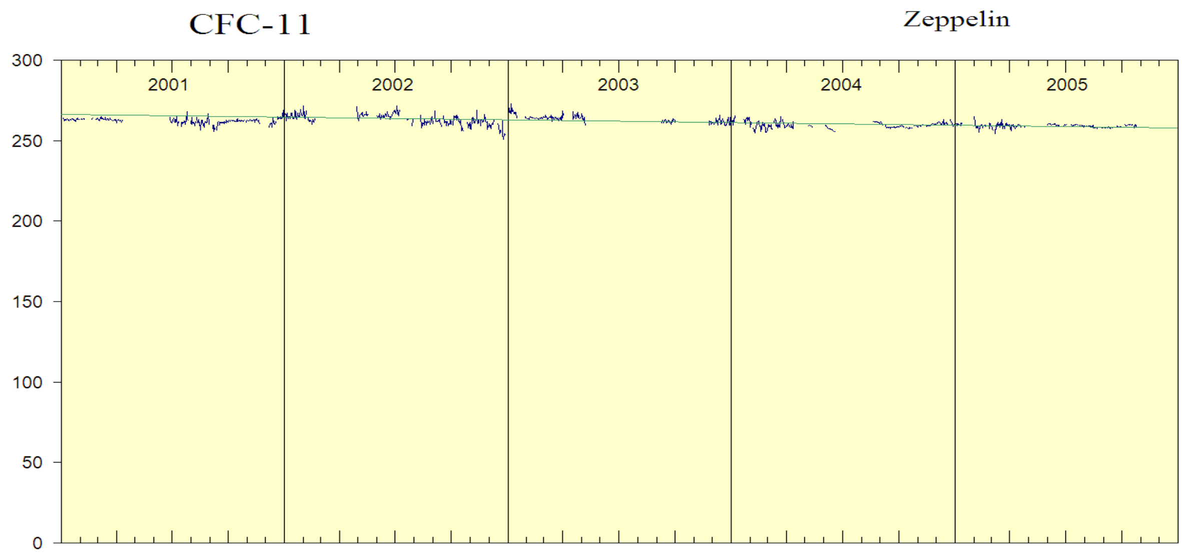


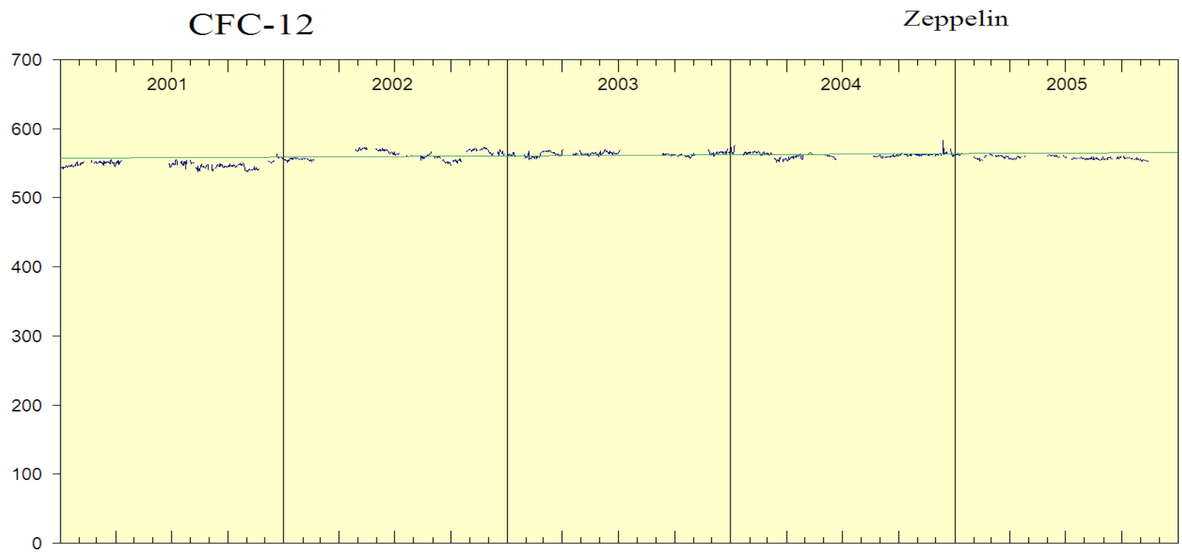



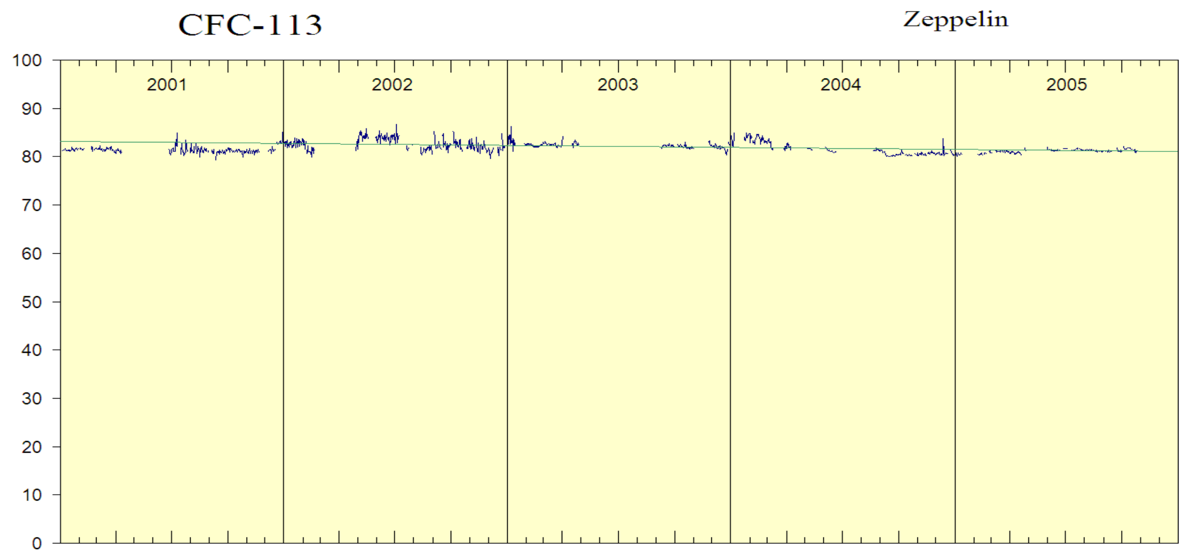



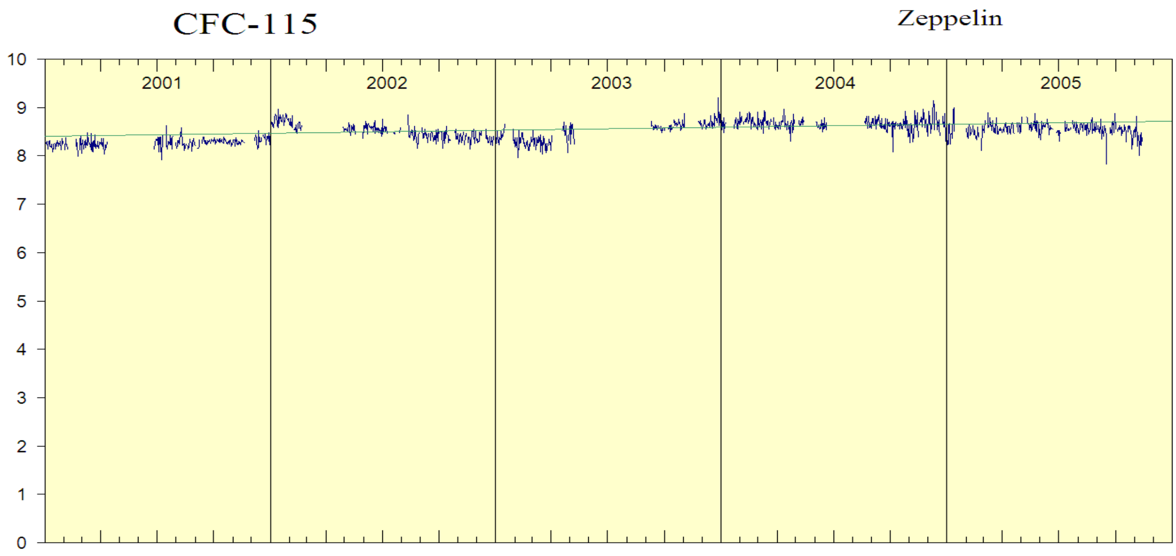

$O_3$ - Ozone
Zeppelin
120
100
80
60
40
20
0
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005

## A.3 Chlorofluorocarbons (CFC)

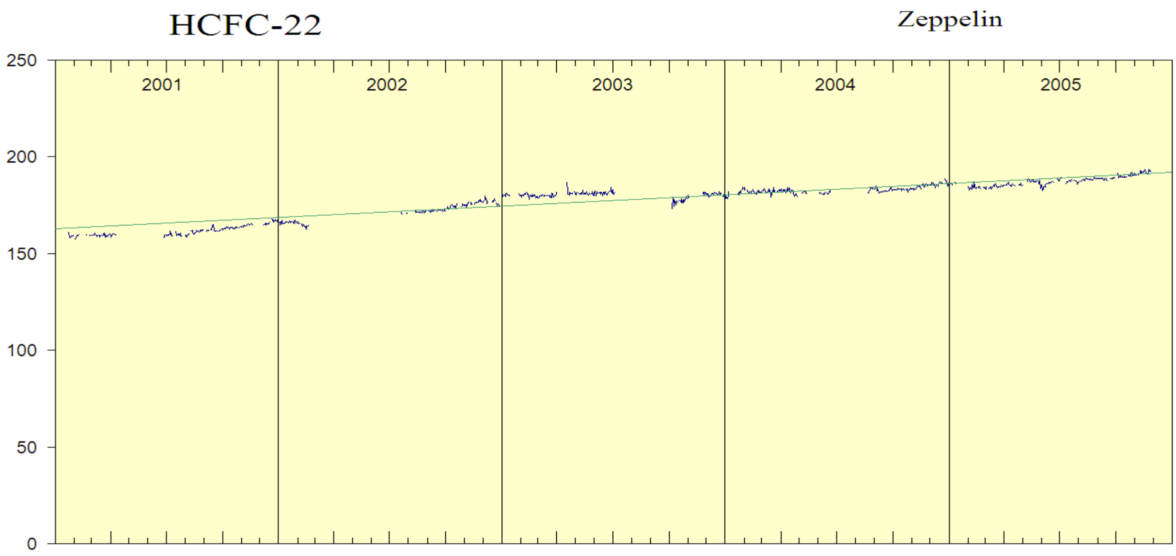


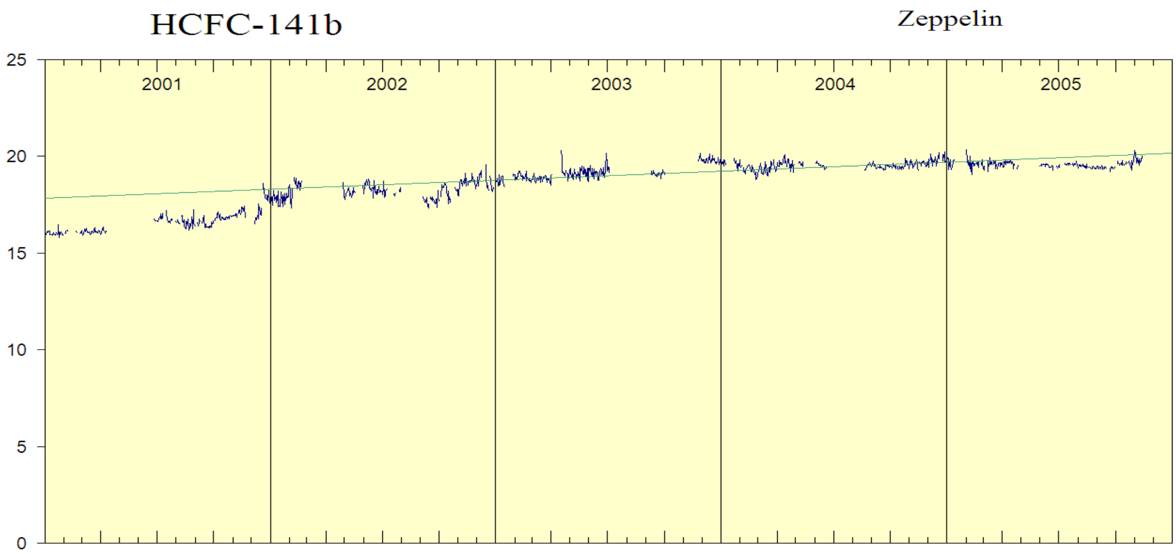



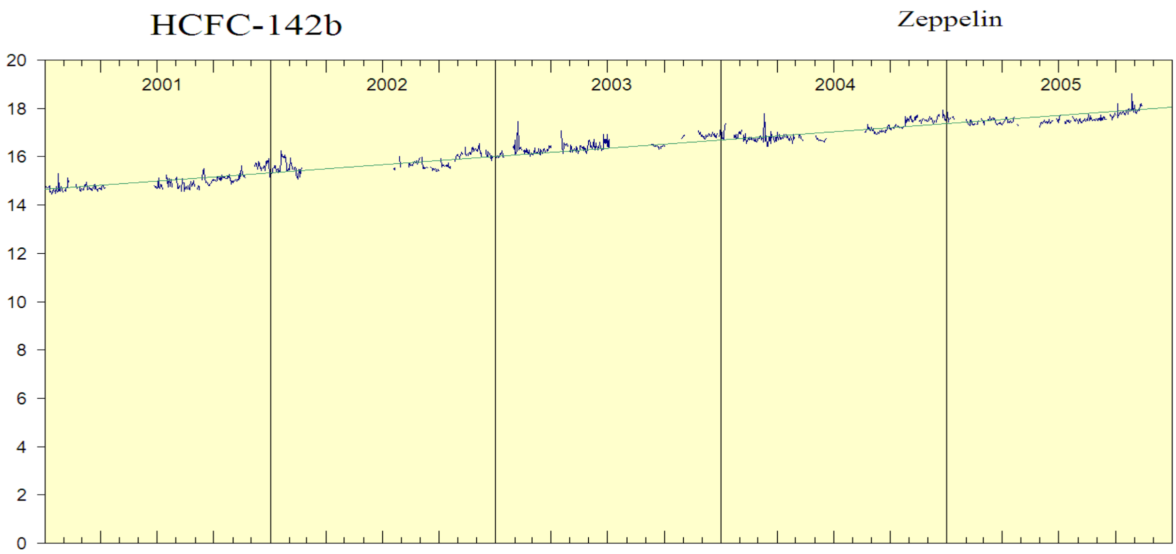




CFC-115
Zeppelin
10
9
8
7
6
5
4
3
2
1
0
2001
2002
2003
2004
2005

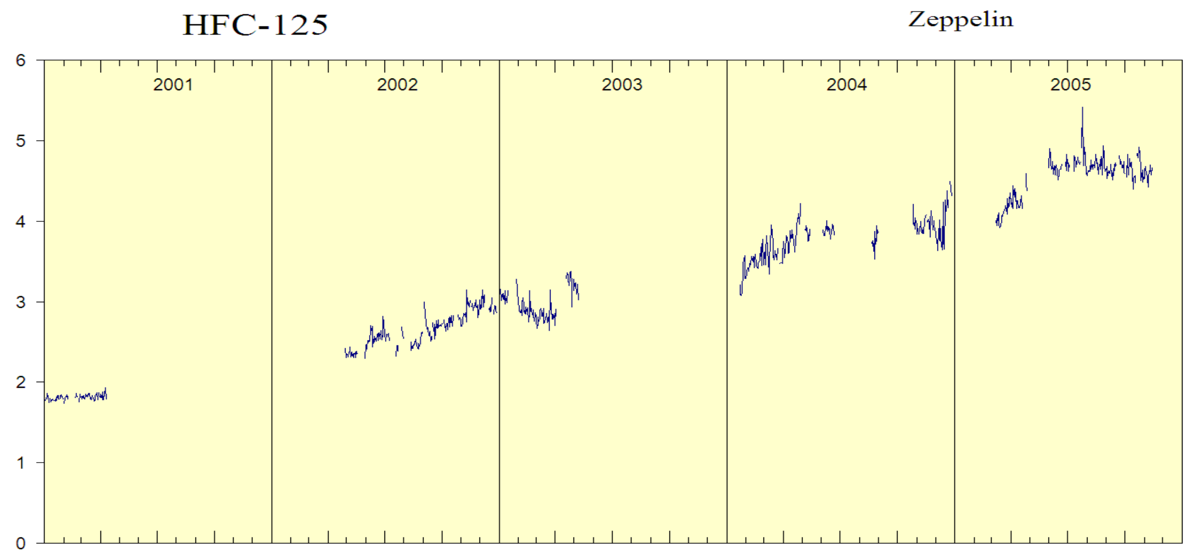
## A.4 Hydrochlorofluorocarbons (HCFC)

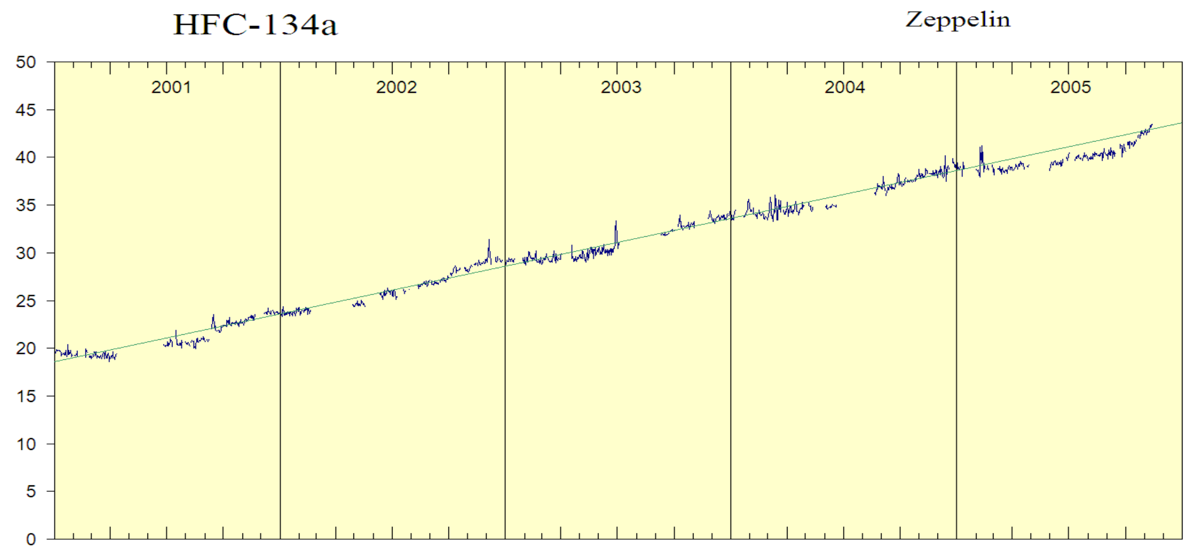


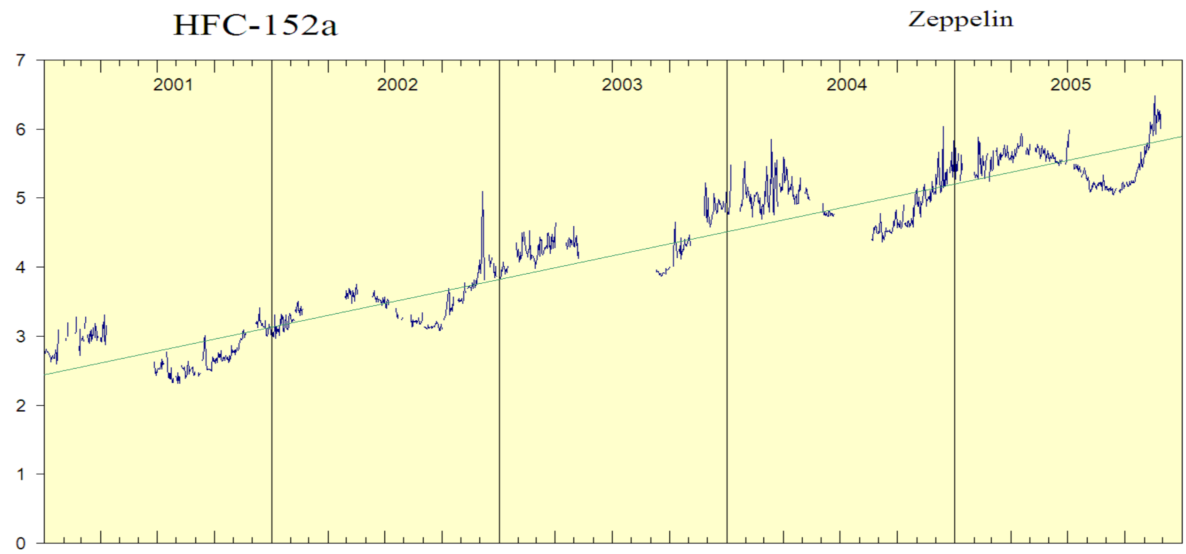



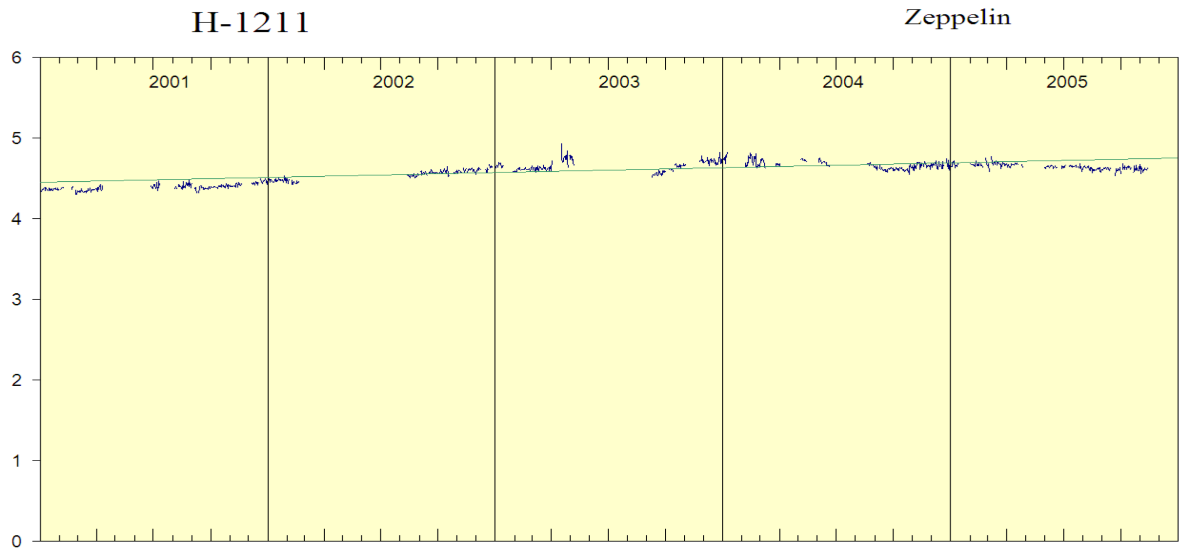
## A.5 Hydrofluorocarbons (HFC)

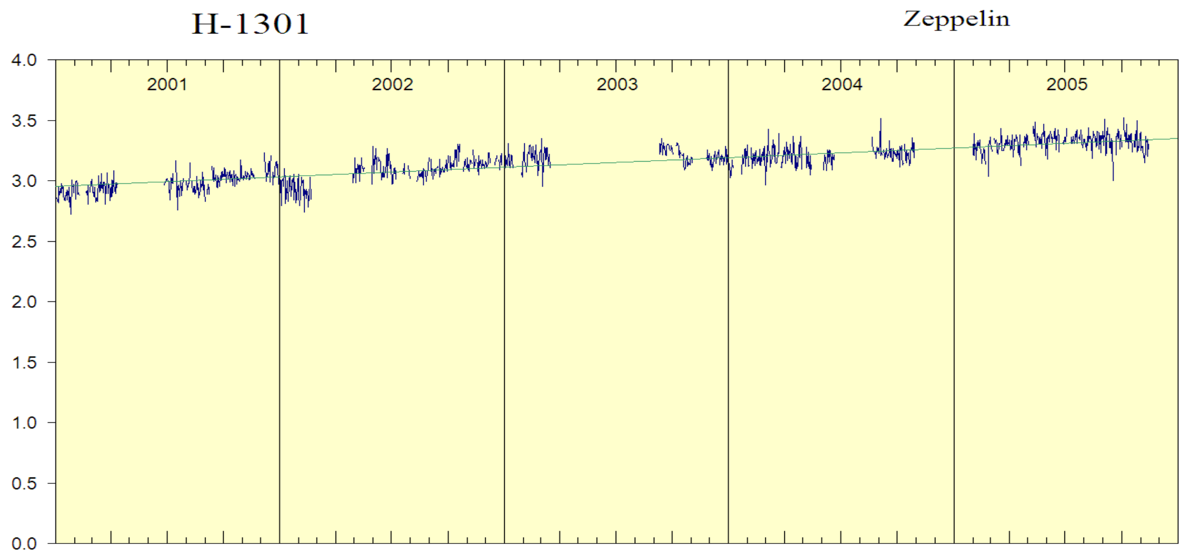


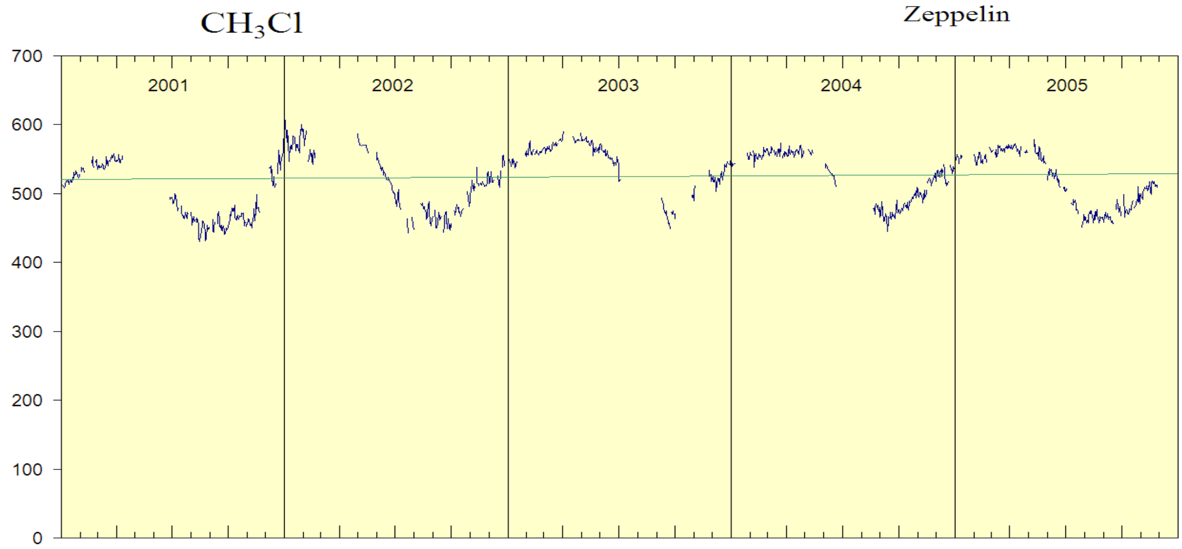



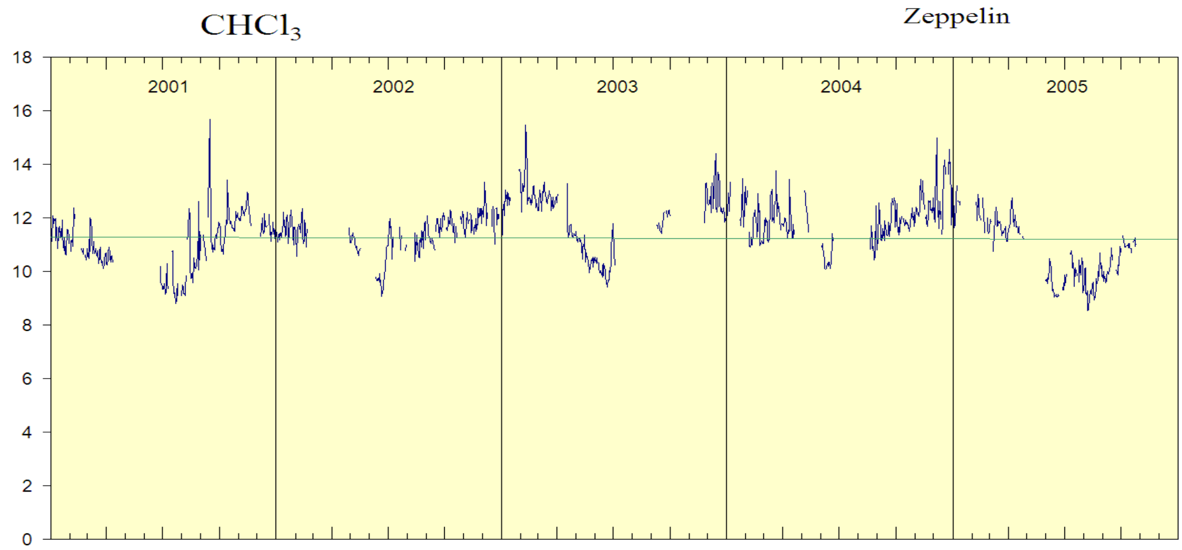
## A.6 Halones

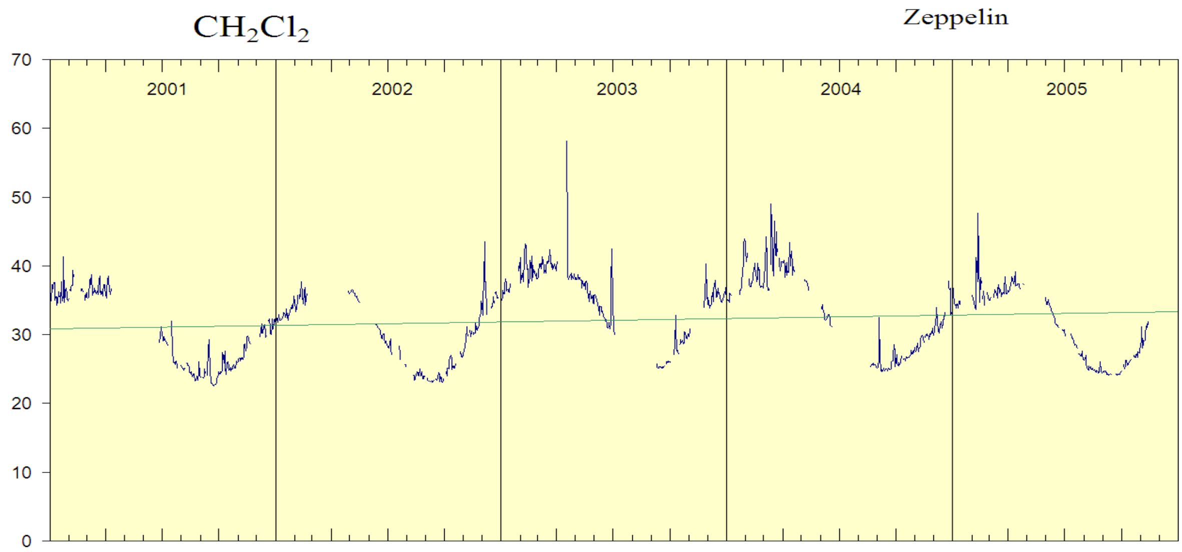

H-1211
Zeppelin
2001
2002
2003
2004
2005
6
5
4
3
2
1
0

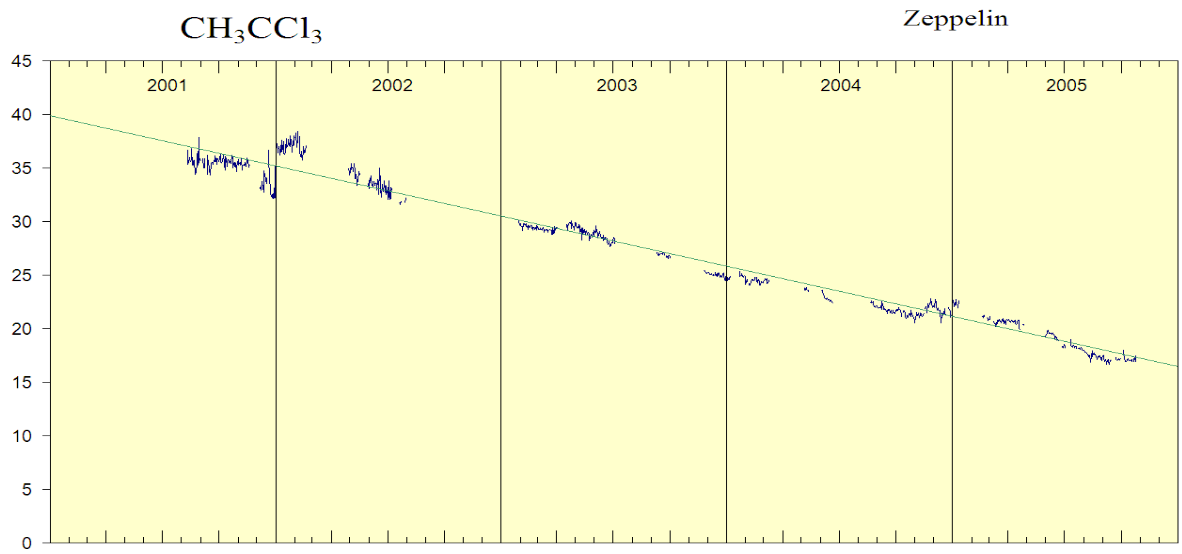

H-1301
Zeppelin
2001
2002
2003
2004
2005
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

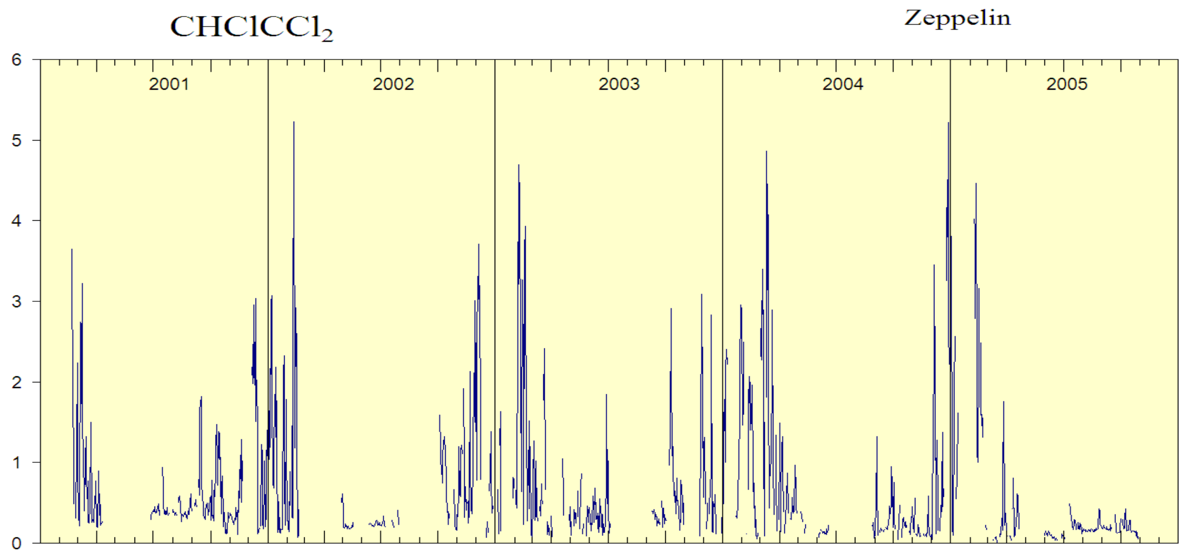
## A.7 Chlorinated compounds

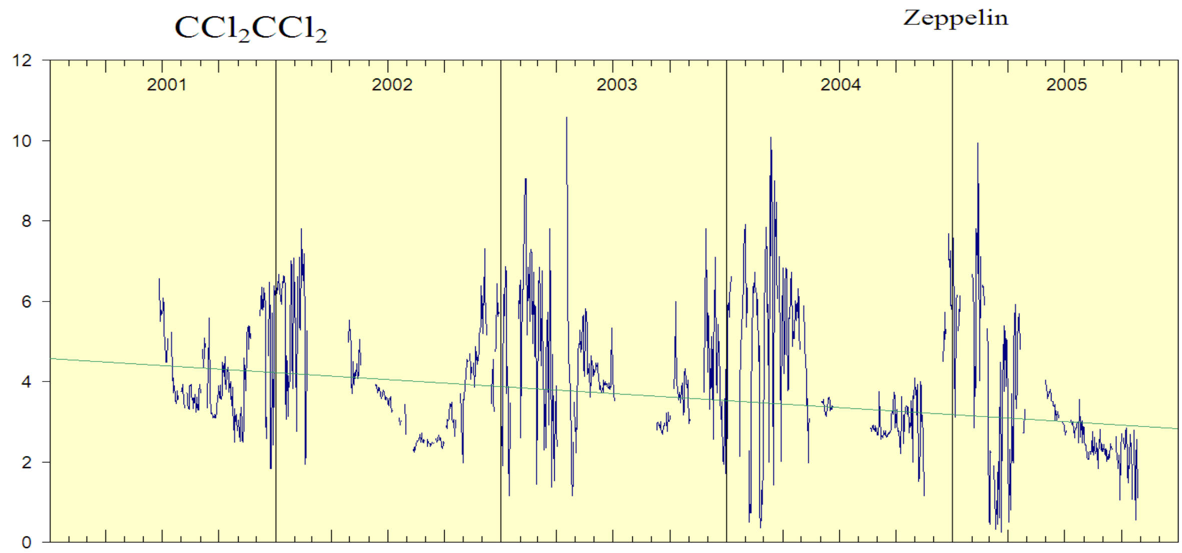


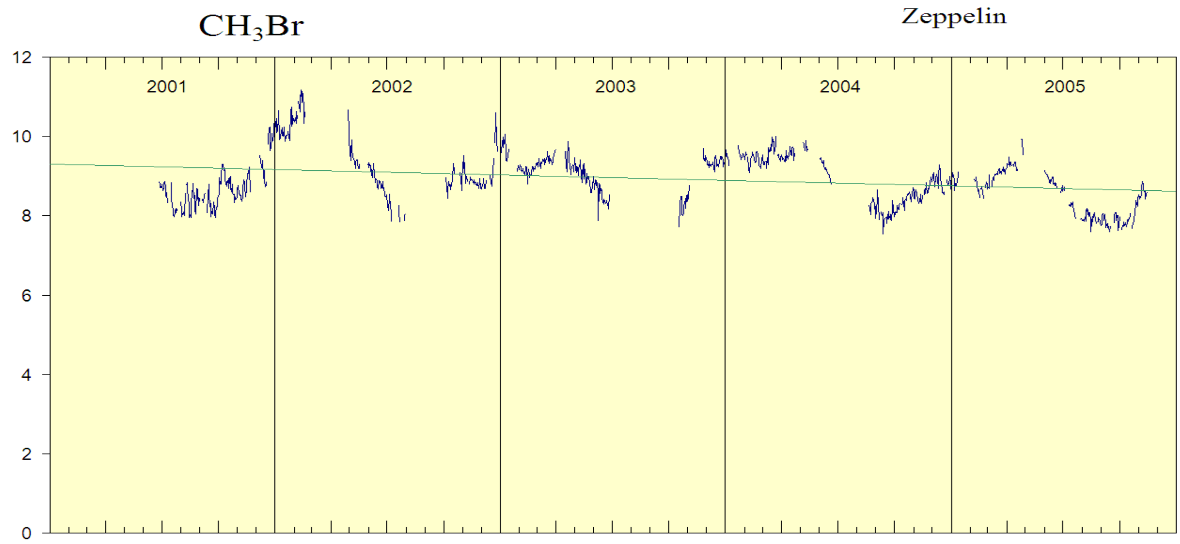



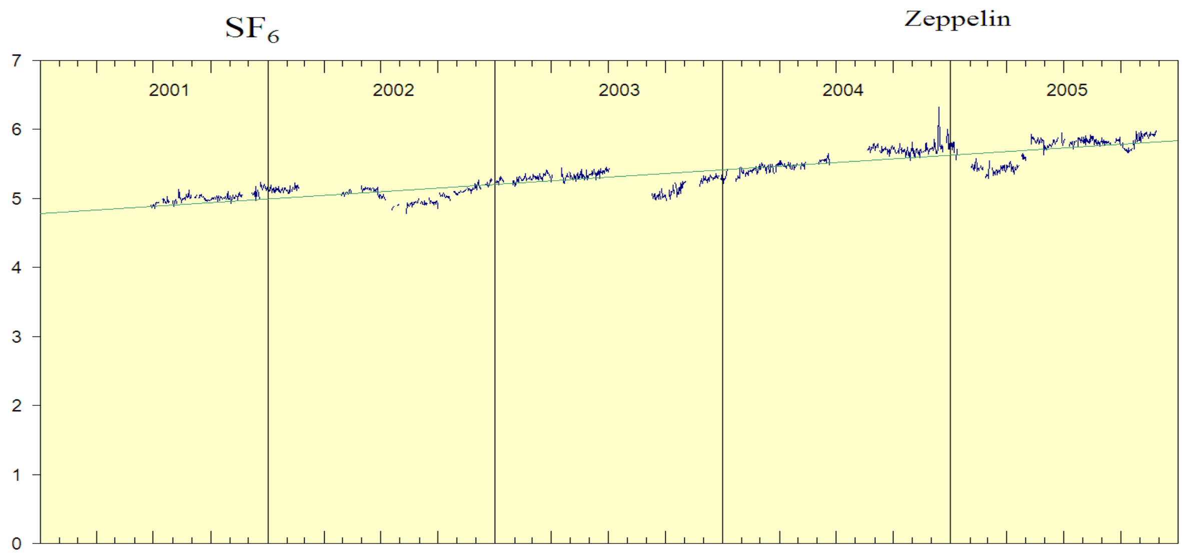

$CH_3CCl_3$
Zeppelin
45
40
35
30
25
20
15
10
5
0
2001
2002
2003
2004
2005


$CHClCCl_2$
Zeppelin
6
5
4
3
2
1
0
2001
2002
2003
2004
2005


$CCl_2CCl_2$
Zeppelin
12
10
8
6
4
2
0
2001
2002
2003
2004
2005

## A.8 Other halogenated compounds



# Appendix B

# Background on the Montreal and Kyoto Protocol

## B.1 Background

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.

## B.2 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 1$^{st}$ 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.

## B.3 Amendments and Adjustments to the Protocol

### B 3.1 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.

### B 3.2 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.

### B 3.3 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.

### B 3.4 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.

### B 3.5 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

## B.4 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 22$^{nd}$ 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.

## B.5 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 $SF_6$.

## B.6 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.

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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 2005.

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 2005


ABSTRACT (in Norwegian)

Rapporten presenterer aktiviteter og måleresultater fra klimagassovervåkingen ved Zeppelinstasjonen på Svalbard i år 2005.

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


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