

**Greenhouse gas monitoring at the Zeppelin station**  
Annual report 2002

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at the Zeppelin station**

**Report  
879/03**

Annual report 2002



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Statlig program for forurensningsovervåking



## Preface

The air monitoring station on the Zeppelin Mountain, close to Ny-Ålesund at Svalbard is situated in an undisturbed arctic environment, away from major pollution sources. This 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 greenhouse gases.

The Norwegian Institute for Air Research (NILU) has a long history of research in Ny-Ålesund. Since 1988, most of these activities have been connected to the research station at the Zeppelin Mountain. Monitoring of climate related factors have been one of NILU's main fields in this work.

In 1999 the Norwegian Pollution Control Authority (SFT) and NILU signed a contract commissioning NILU to run a programme for monitoring of greenhouse gases at the station. 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 measurement programme includes a range of chlorofluorocarbons (CFC), hydrofluorocarbons (HFC), hydrochlorofluorocarbons (HCFC), halones as well as other halogenated organic gases, sulphurhexafluoride (SF<sub>6</sub>), methane (CH<sub>4</sub>) 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<sub>2</sub>) and particles performed by the Department of Meteorology (MISU) and Institute of Applied Environmental Research (ITM) at Stockholm University. These activities are funded by the Swedish Environmental Protection Agency.

Data from the monitoring activities will be 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 2002.



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## Summary

This is an annual report describing the activities in the project *Greenhouse gas monitoring at the Zeppelin station*, year 2002.

A brief description is given on radiative forcing caused by greenhouse gases and aerosols. The report describes the Zeppelin monitoring station and presents some of the activities at the station, as well as current status for instruments and measurement methods used for climate gas monitoring. Results from the measurements are presented as monthly averages and plotted as daily averages.

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<sub>6</sub> and halogenated hydrocarbons including CFC's, HFC's, HCFC's, halones and perfluorocarbons), ozone, aerosols (direct and indirect effects), water vapour and land surface albedo.

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 enabled NILU to broadly 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. Equipment for measurements of halogenated greenhouse gases (CFC's, HFC's, HCFC's, halones, perfluorocarbons and a range of other halogenated hydrocarbons) was installed in the new monitoring station building year 2000 and the extended measurement programme started in the autumn the same year. The measurement programme is continuously extended, with sulphur hexafluoride (SF<sub>6</sub>) as one of the new compounds included in 2001.

Monitoring of methane was started at the Zeppelin station by NILU in 1997. The establishment of the monitoring programme in 1999 enabled NILU to strengthen this activity by increased maintenance and required upgrades of old equipment. This has enhanced the data quality and completeness of the data series.

The measurement programme was further extended in 2001 by installation of instrumentation for monitoring carbon monoxide.

Particles are now monitored continuously at ground level as black carbon. A new Precision-Filter-Radiometer (PFR) sun photometer was installed in 2002 for total column measurements of amount and size distribution of particles. Close contact is established with the Department of Meteorology at Stockholm University, which has been monitoring carbon dioxide since 1989, and Institute of Applied Environmental Research (ITM), which has been monitoring particles since 2000 at the Zeppelin station.

The measurement programme at the Zeppelin station covers all major greenhouse gases except nitrous oxide, one of the strongest contributors to radiative forcing.

Measurements of greenhouse gases 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 may be used for assessment of compliance with the Montreal and Kyoto protocols.

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.

The high frequency of data sampling makes a good basis for the investigation of polluted air transport episodes. Combined with meteorological data and measurements from other European measurement stations, this can be used for the investigation of regional emission inventories.

*Table A: Monthly mean concentration levels of climate gases at the Zeppelin station year 2002. All concentrations in pptv, except for methane (ppb), carbon monoxide (ppb), and carbon dioxide (ppm).*

Compound	Formula	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
<b>Methane</b>	CH <sub>4</sub>	1850	1852			1798	1786	1781	1785	1809	1824	1821	1831	1813
<b>Carbon monoxide</b>	CO	143	150	149	143	124	94	85	93	120	129	135	148	126
<b>Carbon dioxide*</b>	CO <sub>2</sub>	375	376	377	376	376	372	369			371	372	375	374
<b>Chlorofluorocarbons</b>														
CFC-11	CFCl <sub>3</sub>	267	268		271	272	271	266	261	262	265	266	263	267
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	556	555		569	571	568	561	560	554	557	570	565	562
CFC-113	CF <sub>3</sub> Cl	82	81		81	83	83	83	81	82	83	82	82	82
CFC-114	CF <sub>2</sub> ClCF <sub>2</sub> Cl	17.7	17.7		18.1	18.1	18.3	18.2	19	18.2	18.3	18.0	18.3	18.2
CFC-115	CF <sub>3</sub> CF <sub>2</sub> Cl	8.4	8.5		8.6	8.6	8.6	8.7	8.6	8.7	8.6	8.5	8.5	8.6
<b>Hydrofluorocarbons</b>														
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	2.48	2.43		2.34	2.33	2.52	2.48	2.44	2.59	2.65	2.80	2.99	2.55
HFC-134a	CF <sub>3</sub> CH <sub>2</sub> F	23.9	24.0		24.7	24.8	25.8	25.8	26.8	27.1	28.2	28.9	29.5	26.3
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	3.1	3.2		3.5	3.6	3.6	3.3	3.1	3.1	3.4	3.7	4.0	3.4
<b>Hydrochlorofluorocarbons</b>														
HCFC-22	CHF <sub>2</sub> Cl	163	164		164	166	168	165	166	167	169	171	171	167
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	1.12	1.08		1.14	1.08	1.12	1.05	0.94	0.99	1.05	1.06	1.08	1.06
HCFC-124	CHFClCF <sub>3</sub>	1.66	1.66		1.70	1.68	1.70	1.66	1.70	1.69	1.68	1.69	1.71	1.69
HCFC-141b	CH <sub>3</sub> CFCl <sub>2</sub>	18.9	19.4		19.5	19.1	19.6	19.2		18.9	19.0	19.0	19.2	19.2
HCFC-142b	CH <sub>3</sub> CF <sub>2</sub> Cl	15.4	15.4		16.1	15.9	15.9	15.6	15.7	15.5	15.7	16.2	16.2	15.8
<b>Halons</b>														
H-1301	CF <sub>3</sub> Br	2.95	2.89		3.05	3.08	3.14	3.24	3.23	3.27	3.32	3.29	3.30	3.16
H-1211	CF <sub>2</sub> ClBr	4.46	4.44						4.51	4.54	4.54	4.56	4.57	4.52
<b>Halogenated compounds</b>														
Methylchloride	CH <sub>3</sub> Cl	572	571		586	570	525	473	472	459	475	511	522	521
Methylbromide	CH <sub>3</sub> Br	10.2	10.7		10.8	9.7	8.9	7.8	10.0	9.1	8.7	8.6	8.7	9.4
Methyl iodide	CH <sub>3</sub> I	0.3	0.6		1.2	1.0	1.0	0.8	1.5	0.7	1.0	0.9	0.9	0.9
Methylendichloride	CH <sub>2</sub> Cl <sub>2</sub>	32.8	35.2		34.7	33.9	31.0	26.7	23.5	22.7	25.5	30.2	34.6	30.1
Chloroform	CHCl <sub>3</sub>	11.3	11.4		10.9	10.5	9.8	10.9	10.8	11.1	11.8	11.9	12.0	11.1
Methylchloroform	CH <sub>3</sub> CCl <sub>3</sub>	31.7	32.0		34.2	33.8	32.5	29.8						32.4
Carbontetrachloride	CCl <sub>4</sub>	94	97		99	98	97	92	90	87	91	93	92	94
Perchloroethylene	C <sub>2</sub> Cl <sub>4</sub>	5.6	5.6		5.3	4.4	4.2	3.3	2.5	2.5	3.0	4.5	5.2	4.2
Sulphurhexafluoride	SF <sub>6</sub>	5.2	5.2		5.1	5.1	5.1	5.0	4.9	4.9	4.9	5.0	5.0	5.0

\*Measurements of CO<sub>2</sub> performed by MISU.

# 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 preindustrial time, are indicated in Figure 1.

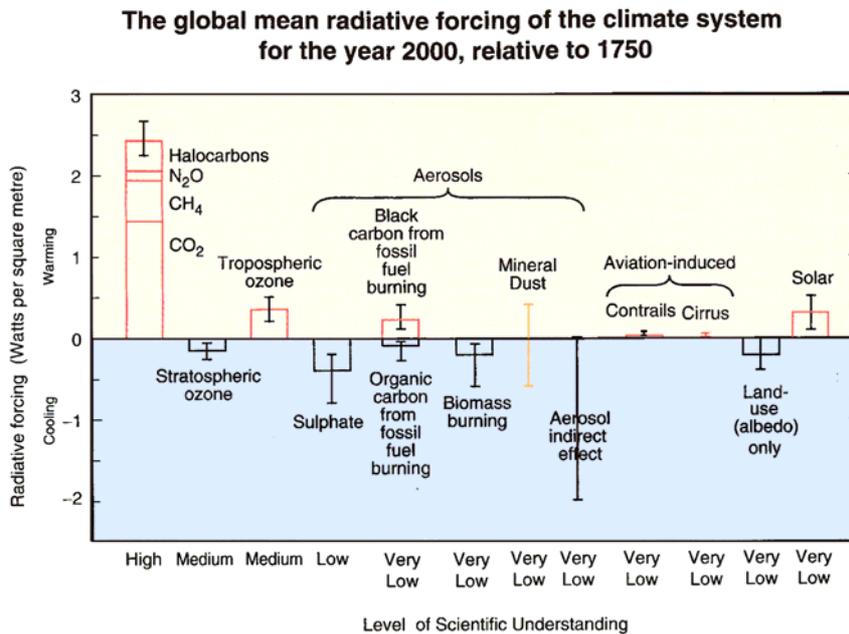


Figure 1: Known factors and their influence on radiative forcing relative to preindustrial time. The vertical lines indicate the uncertainties for each factor. (Source: IPCC.)

## 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<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). 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<sub>2</sub> 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<sub>4</sub> 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<sub>4</sub> concentration. This is caused by CO reacting with reactive OH, thus preventing OH from reacting with CH<sub>4</sub>, a primary loss reaction for methane (ref. Daniel, Solomon).

The atmospheric concentration of N<sub>2</sub>O 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.

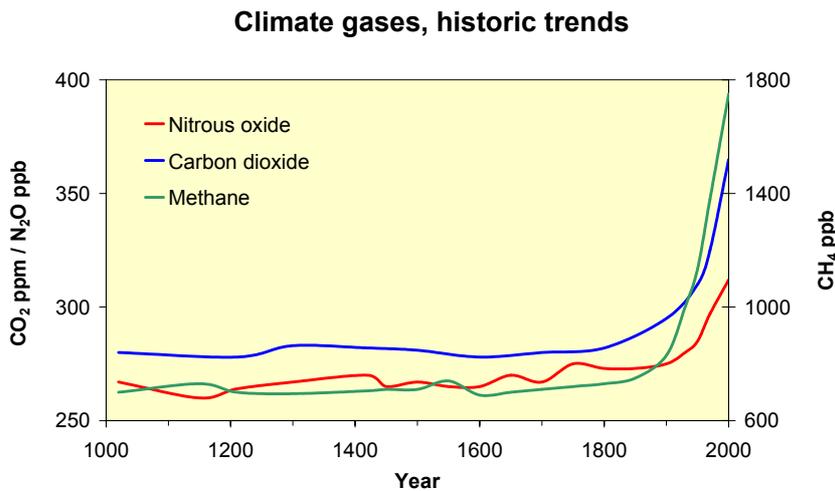


Figure 2: Changes in concentration levels over time for some natural climate gases.

Ozone (O<sub>3</sub>) is a reactive gas with relatively large variation in concentration levels. The amount of tropospheric O<sub>3</sub> has increased by 35% since 1750, mainly due to anthropogenic emissions of O<sub>3</sub>-forming gases like volatile organic compounds (VOCs), carbon monoxide (CO) and nitrogen oxides. O<sub>3</sub> 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<sub>2</sub>O is the oxidation of CH<sub>4</sub> and possibly future direct injection of H<sub>2</sub>O 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<sub>6</sub> and halons. These gases did not exist in the atmosphere before the 20<sup>th</sup> 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: Global warming potential for some selected greenhouse gases (source: IPCC, 2001).

Compound	Formula	Abundance* ppt	Trend ppt/year*	Annual emission	Lifetime, years	GWP <sup>1</sup> 100-year
<b>Non-halogenated compounds</b>						
Carbon dioxide***	CO <sub>2</sub>	367	~1.5	~8 PgC		1
Methane**	CH <sub>4</sub>	1745	7	600 Tg	8.4/12	23
Nitrous oxide**	N <sub>2</sub> O	315	0.8	16.4 TgN	120/114	296
Carbon monoxide**	CO	80	6	~2800 Tg	0.08-0.25	
<b>Chlorofluorocarbons</b>						
CFC-11	CFCl <sub>3</sub>	268	-1.4		45	4 600
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	533	4.4		100	10 600
CFC-13	CF <sub>3</sub> Cl	4	0.1		640	14 000
CFC-113	CF <sub>3</sub> Cl	84	0.0		85	6 000
CFC-114	CF <sub>2</sub> ClCF <sub>2</sub> Cl	15	<0.5		300	9 800
CFC-115	CF <sub>3</sub> CF <sub>2</sub> Cl	7	0.4		1 700	7 200
<b>Hydrofluorocarbons</b>						
HFC-23	CHF <sub>3</sub>	14	0.55	~7 Gg	260	12 000
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>				29	3 400
HFC-134a	CF <sub>3</sub> CH <sub>2</sub> F	7.5	2.0	~25 Gg	13.8	1 300
HFC-143a	CH <sub>3</sub> CF <sub>3</sub>				52	4 300
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	0.5	0.1	~4 Gg	1.4	120
<b>Hydrochlorofluorocarbons</b>						
HCFC-22	CHF <sub>2</sub> Cl	132	5		11.9	1 700
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>				1.4	120
HCFC-124	CHFClCF <sub>3</sub>				6.1	620
HCFC-141b	CH <sub>3</sub> CFCl <sub>2</sub>	10	2		9.3	700
HCFC-142b	CH <sub>3</sub> CF <sub>2</sub> Cl	11	1		19	2 400
<b>Halons</b>						
H-1301	CF <sub>3</sub> Br	2.5	0.1		65	6 900
H-1211	CF <sub>2</sub> ClBr	3.8	0.2		11	1 300
H-2402	CF <sub>2</sub> BrCF <sub>2</sub> Br	0.45	~0		<20	
<b>Other halogenated compounds</b>						
Methylchloride	CH <sub>3</sub> Cl				1.3	16
Methylbromide	CH <sub>3</sub> Br				0.7	5
Methyliodide	CH <sub>3</sub> I					
Methylenedichloride	CH <sub>2</sub> Cl <sub>2</sub>				0.46	10
Methylenedibromide	CH <sub>2</sub> Br <sub>2</sub>				0.41	1
Chloroform	CHCl <sub>3</sub>				0.51	30
Bromoform	CHBr <sub>3</sub>					
Methylchloroform	CH <sub>3</sub> CCl <sub>3</sub>	69	-14		4.8	140
Carbontetrachloride	CCl <sub>4</sub>	102	-1.0		35	1 800
Trichloroethylene	CHCl <sub>3</sub>					
Perchloroethylene	C <sub>2</sub> Cl <sub>4</sub>					
1,2-Dichloroethane	CH <sub>2</sub> ClCH <sub>2</sub> Cl					
Perfluoromethane	CF <sub>4</sub>	80	1.0	~15 Gg	>50 000	5 700
Perfluoroethane	C <sub>2</sub> F <sub>6</sub>	3.0	0.08	~2 Gg	10 000	11 900
Sulphurhexafluoride	SF <sub>6</sub>	4.2	0.24	~6 Gg	3 200	22 200

\*Global mixing ratios 1998 (ppt = parts per trillion). \*\*Concentration levels and trends in ppb and ppb/year (ppb = parts per billion).

\*\*\*Concentration levels and trends in ppm and ppm/year (ppm = parts per million). <sup>1</sup>Global warming potential relative to CO<sub>2</sub>.

## 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 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 MISU (Meteorological Institution Stockholm University).

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 MISU, 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 station is part of the EU-financed Large Scale Facility for Arctic Environmental Research, resulting in a number of visiting scientists and research groups.

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)
- 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 amount and size distribution through a total column.

The station at Zeppelin is also used for a long range of measurements not directly related to climate gas monitoring, including daily measurements of sulphur and nitrogen compounds ( $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $(\text{NO}_3^- + \text{HNO}_3)$  and  $(\text{NH}_4^+ + \text{NH}_3)$ ), main compounds in precipitation, mercury, persistent organic pollutants (HCB, HCH, PCB, DDT, PAH etc.), as well as tropospheric and stratospheric ozone.

### **2.2.2 MISU and ITM**

MISU (Department of Meteorology at Stockholm University) measure carbon dioxide ( $\text{CO}_2$ ) and together with ITM (Institute of Applied Environmental Research) atmospheric particles on the Zeppelin Mountain.

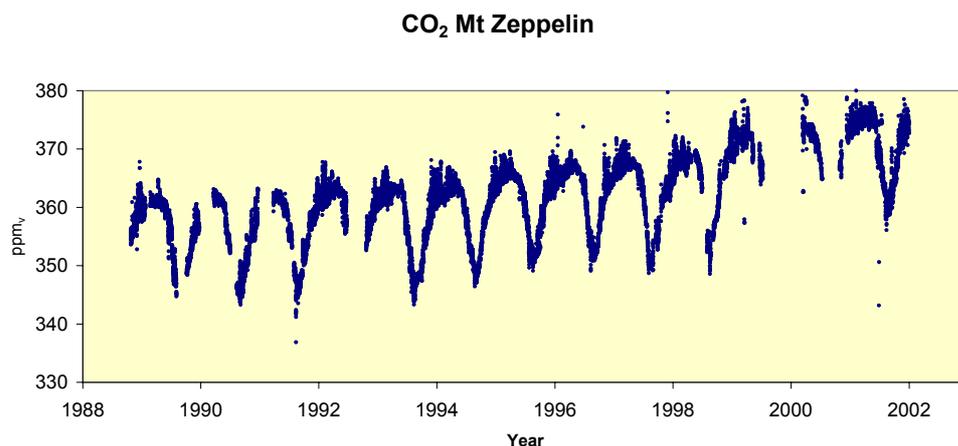
MISU maintains a continuous infrared  $\text{CO}_2$  instrument on the Zeppelin Mountain. The continuous data are enhanced by weekly flask sampling programmes in co-operation with other institutions. The flask data give  $\text{CO}_2$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $\text{CH}_4$  and CO data.

The CO<sub>2</sub> monitoring project at the Zeppelin station has three goals:

- provide a baseline measurement of European Arctic CO<sub>2</sub> concentrations
- allow detailed analysis of the processes behind CO<sub>2</sub> 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<sub>2</sub> and CH<sub>4</sub>.

MISU and ITM have 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) operated by ITM gives the concentration of aerosol particles and, combined with data from the nephelometer (MISU), clues to the particles' age and origin. Size distribution is acquired from a differential mobility analyser (DMA), operated by ITM.

Understanding atmospheric chemical processes requires more than just CO<sub>2</sub> and aerosols and scattering data. A total filter allows to create a bi-daily record of the chemical composition of aerosol particles.



*Figure 4: MISU have been measuring CO<sub>2</sub> 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 on glass canisters and sent to be analysed in the laboratories at Boulder, Colorado in USA. The measurement programme includes CH<sub>4</sub>, CO, H<sub>2</sub>, N<sub>2</sub>O and SF<sub>6</sub>. Results from the analysis are used in studies of trends, seasonal variations and global distribution of greenhouse gases.

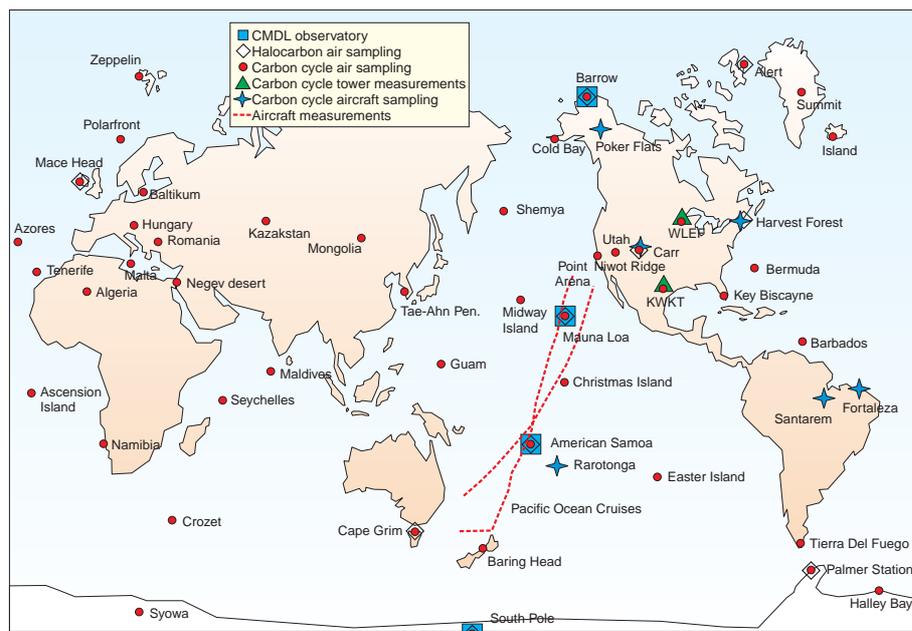


Figure 5: NOAA's global air sampling network.

### 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 will be 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.

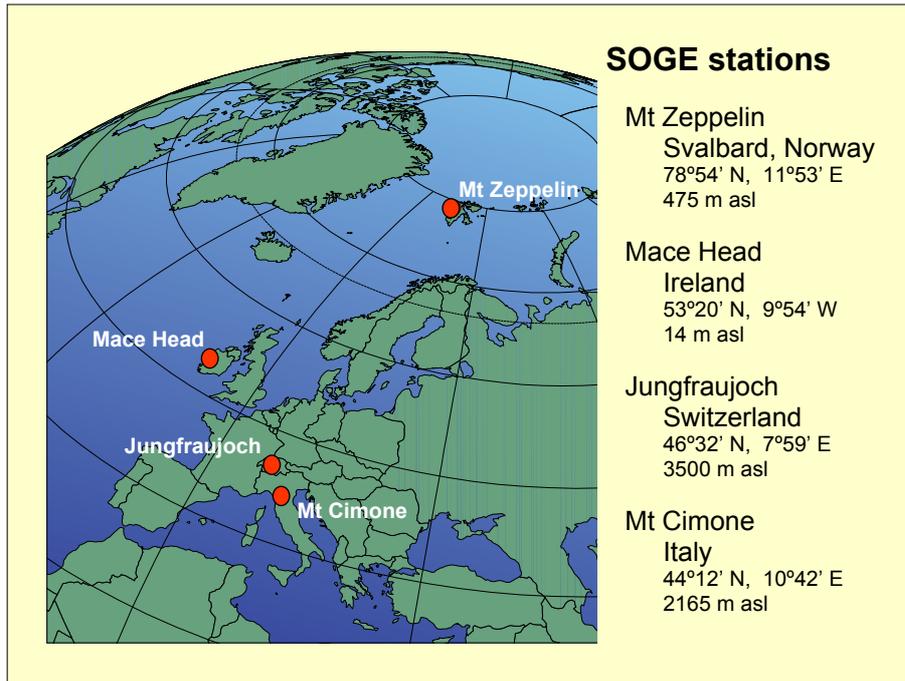


Figure 6: The SOGE climate gas monitoring stations.

### 3. Measurements

#### 3.1 Instruments and methods

##### 3.1.1 Halocarbons

Measurements of volatile halocarbons started in late spring 2000, when a specially designed instrument was installed. 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<sub>4</sub>, CO and CO<sub>2</sub> in Table 2.

A fully automated adsorption/desorption device is used for pre concentration of 2000 ml air over a time period of 40 minutes. The compounds are then separated and detected by the use of an automatic gas chromatograph with a mass spectrometric detector (GC-MS). The total analysis time is 2 hours. Each air sample run is followed by analysis of air from a pressurized cylinder, which is used as working standard. The four sites within the SOGE project are using working standards, which are pressurized simultaneously at Mace Head and then calibrated to AGAGE (Advanced Global Atmospheric Gases Experiment) scale before shipment to the individual sites. After about four months of use they are shipped back to the laboratory in Bristol for end calibration. This final calibration of the working standard is used together with the initial concentration to define the concentrations of the air samples analysed within this time period.

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. In the data network from all stations, data are accessible for each participant one day after the measurements are performed.

Instrumental problems in April/May 2002 resulted in a period of almost two months of data loss due to delivery problems of spare parts. There have been short interruptions in the measurements due to periodical maintenance, but the overall data coverage is considered to be good for the year 2002.

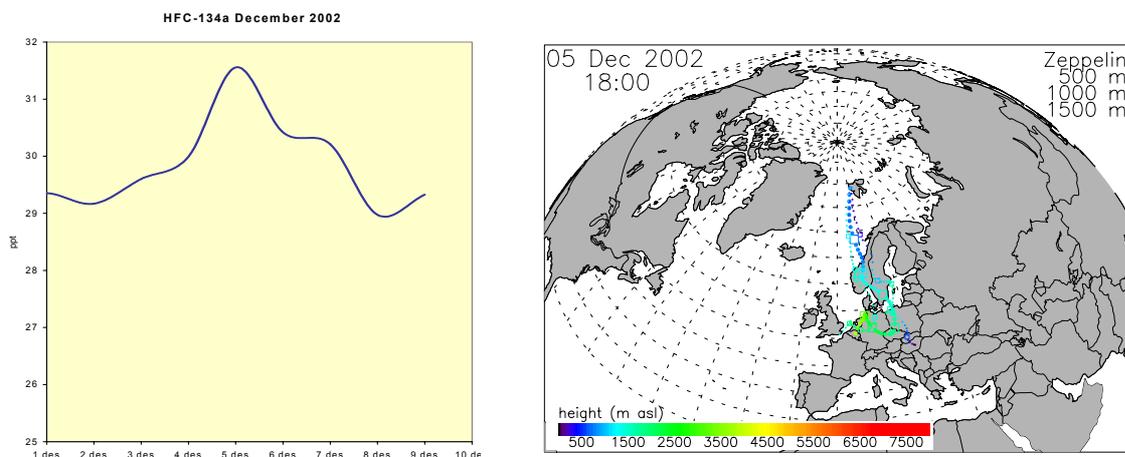


Figure 7: A typical episode of increased levels of several halogenated compounds occurred on 5 December 2002. Trajectories from the same day indicate transport of air masses from the European continent.

### 3.1.2 Methane

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 is quite old and there have been some problems with valve switching and detector function, resulting in a period of reduced data availability in January 2002 and first half of August 2002. Problems with the detector from February to April 2002 resulted in a period of lost data. However, it is expected that an almost complete data series can be recovered when transferred to the new data system

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. The upgrade was expected to take place in September 2001, but has been further delayed from the supplier. All methane data will be recalculated when this system is in place.

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.

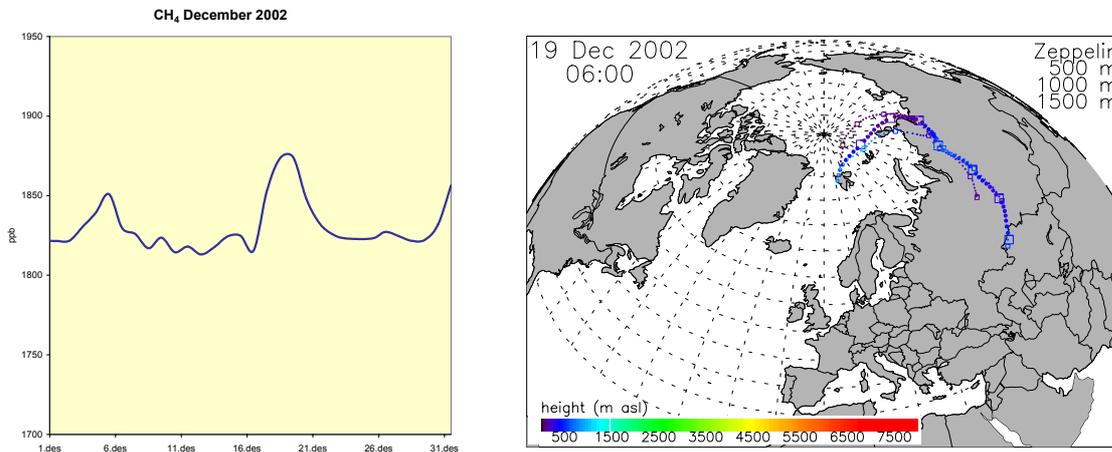


Figure 8: Among few methane episodes during 2002, there are three clear incidents during the month of December. The highest values were measured on 19 December where trajectories indicate transport of air masses from Siberia, Russia.

### 3.1.3 Carbon Monoxide

NILU's CO instrument was reinstalled at the Zeppelin station 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 conclusions referred to for the methane instrument (above) also apply for the CO-instrument.

The instrument is an automatic gas chromatograph with mercury oxide reduction followed by UV detection. It has been running without interruptions since installation. The instrument is connected to the same system for data collection as the methane instrument and will use the new upgraded system from Scripps for data handling.

The instrument is performing analysis of 5 air samples and one standard within a time period of 2 hours. The standard is calibrated directly to the Mace Head standards, which are part of AGAGE.

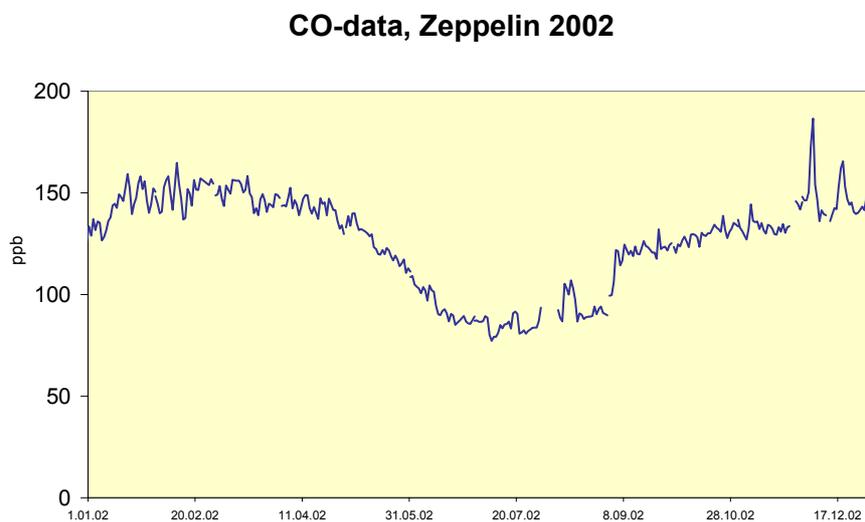


Figure 9: Plot of CO-measurement data at the Zeppelin-station. The plot shows an expected seasonal variation in concentration level.

### 3.1.4 Sun photometer measurements at Ny-Ålesund

A new sun photometer for measurements of particles was installed in Ny-Ålesund in the end of April 2002. The instrument use the sun as a light source and measures the total amount of particles in a column from the ground up through the atmosphere. The use of the sun as a light source limits the periods for data capture since measurements can only be performed on clear days during the arctic summer.

The sun photometer at Ny-Ålesund is a Precision-Filter-Radiometer (PFR) that accurately measures direct solar radiation in four wavelengths; 368, 411, 501, and 862 nm. The sun photometer is directed towards the sun and follows the sun across the sky during the day. The signals that are recorded every minute are the averages of ten single measurements taken within 1.25 second. The aerosol optical densities (AOD) at the four wavelengths are important parameters for aerosol optical characterisation that can be compiled from the sun photometer measurements. The precipitable water amount (PW) is another important

parameter for aerosol optical characteristics that can be measured with sun photometers at 936 nm, but this is not measured at Spitsbergen. The sun photometer at Ny-Ålesund is part of a large global network AERONET run by Goddard Space Flight Center under NASA (<http://aeronet.gsfc.nasa.gov/>) with routine observations that are important for the assessment of the global radiation budget and climate change in combination with satellite measurements.

Haze and visibility degradation is due to scattering and absorption of visible light by gases and airborne particles, and scattering being more important than absorption. Scattering of sunlight by the permanent gases of air, the Rayleigh scattering, is the largest single physical process reducing the light intensity at the sun photometer in Ny-Ålesund. The scattering by particles in the visible part of the spectrum, 0.4 – 0.7  $\mu\text{m}$ , is more efficient for short wavelengths than for longer. The particle size with the largest contribution to the scattering at a wavelength  $\lambda$  is given by  $r/\lambda \approx 0.5$  where  $r$  is the particle radius according to Junge (1963). The only gas absorption of light significant to the sun photometer results at Ny-Ålesund is by ozone, mostly at 501 nm. The variation in the  $\text{O}_3$  column content during the measurement period has not been taken into account in the results below, with 320 D.U. used in the calculations. AOD is the scattering due to airborne particles and depends on the particle amount in a column from the instrument ( $\sim$  sea level) to the top of the atmosphere directed towards the sun. The AOD that can be determined from the sun photometer measurements will obtain different values at different light wavelengths due to the scattering's dependence on the particles size. It should be kept in mind the AOD is estimated as the difference between the total scattering and the Rayleigh scattering, i.e. it is at Spitsbergen a fairly small difference between to large numbers, and will therefore contain a certain uncertainty.

A sun photometer needs a clear sky towards the sun in order to give useful data, and this limits the data capture at Ny-Ålesund. The photometer measurements were started 1<sup>st</sup> May and the photometer was operated until 15<sup>th</sup> October, and giving useful data from 66 days only. On clear days during the Arctic summer the photometer on the other hand, in principle, could measure both day and night due to the midnight sun.

Figure 10 gives the monthly AOD arithmetic averages of all accepted measurements during 2002. A high AOD indicates a high number of particles, and the results from Ny-Ålesund are generally very low indicating low concentrations of particles in the atmosphere there. The AOD at a short wavelength is normally higher than that measured at a longer wavelength, indicating that the number of small particles is the largest. According to Junge most of the scattering is due to particles between about 0.4 – 0.8  $\mu\text{m}$  at the wavelengths applied at Ny-Ålesund.

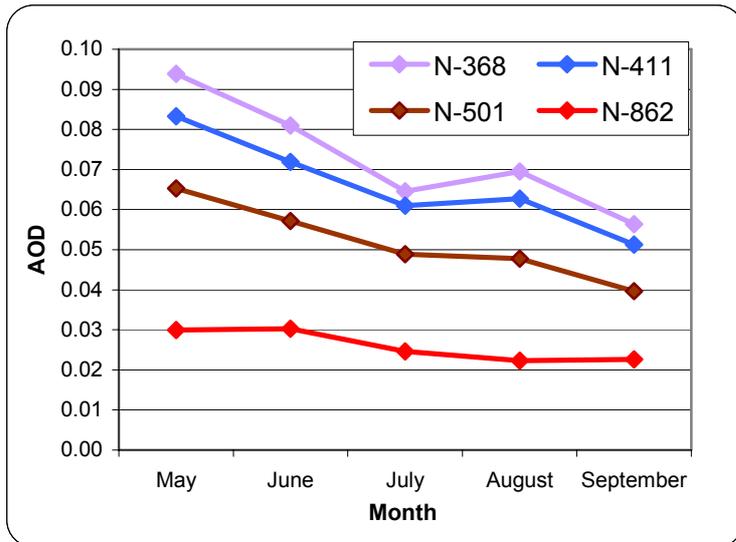


Figure 10: Monthly average AOD at 368, 411, 501, and 862 nm during May – September 2002 at Ny-Ålesund.

The aerosol number concentration is low at Spitsbergen compared to continental sites with larger emissions and production of particles. Figures 11a and 11b compares the AOD results from Ny-Ålesund with corresponding measurements at Gotland in Sweden and measurements at the Joint Research Centre at Ispra near Lago Maggiore in northwestern Italy. The wavelengths compared are nearly, but not quite identical. Gotland is located in the Baltic Sea while the Ispra site in northern Italy at Lago Maggiore is a region with considerable anthropogenic activities and correspondingly high gas and particle concentrations. Both locations are regular EMEP sites. Both the number of measurements and measurement days are different making a direct comparison of the AOD at the sites difficult, but the results indicate a factor of ten between Ispra and Ny-Ålesund while Gotland, as expected in-between.

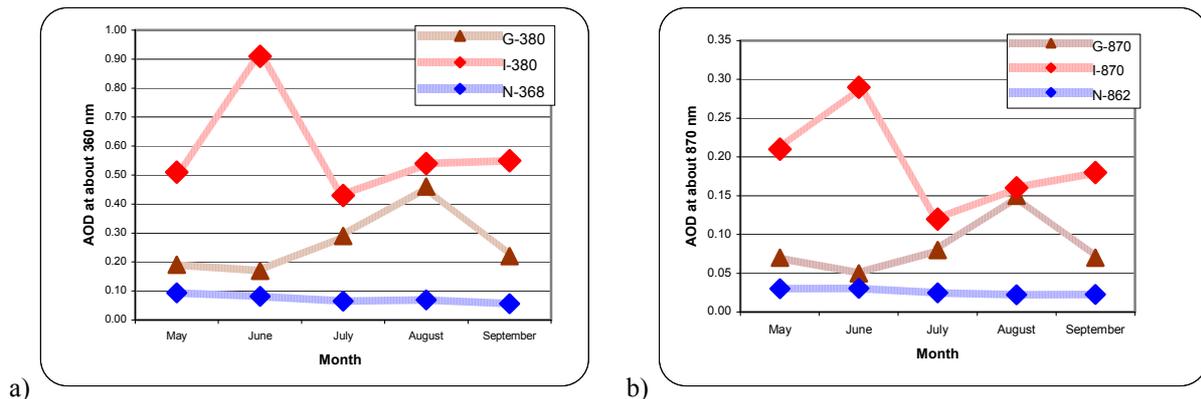


Figure 11a and b: Monthly averages of AOD at Gotland (G-380/870) and Ispra (I-370/860) at 380 nm and 870 nm, with Ny-Ålesund (N-368/862) at 360 nm and 862 nm.

The Ångström exponent,  $\alpha$ , that can be calculated from the AOD, is sensitive to the aerosol size distribution. A small  $\alpha$  indicates a high number of the larger particles; normally this exponent will vary between 2.0 and 0.5. A time series of  $\alpha$  will therefore give information on

the variation in the particle size distribution during the measurement period. Figure 12 presents the daily averages of Ångström's  $\alpha$ , which in general are higher than 0.5 except for 16th September. The corresponding AOD in Figure 13 show an increase in the AOD at 863 nm on that day, indicating a shift in the particle size distribution with larger particles passing the column from the morning culminating at 10 GMT.

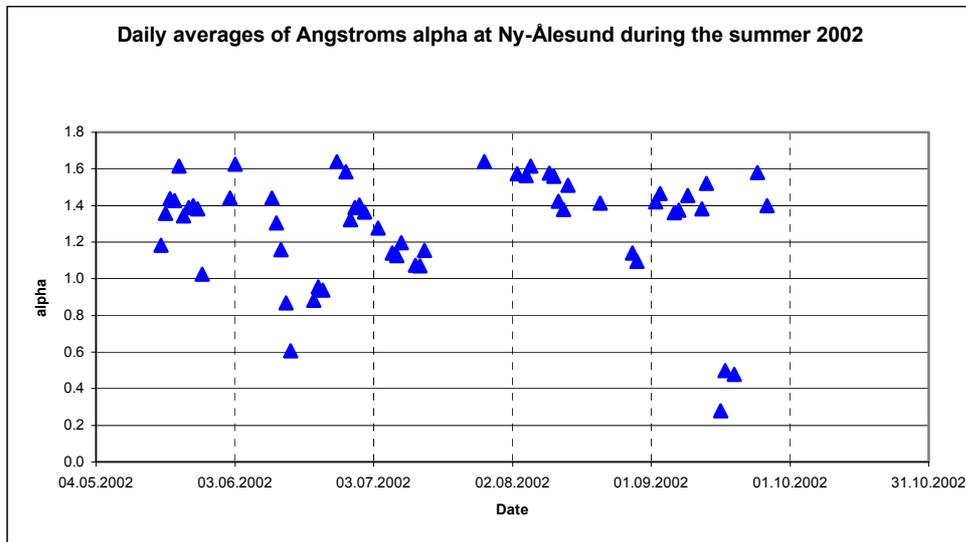


Figure 12: Daily averages of Ångström  $\alpha$  at Ny-Ålesund during the summer 2002.

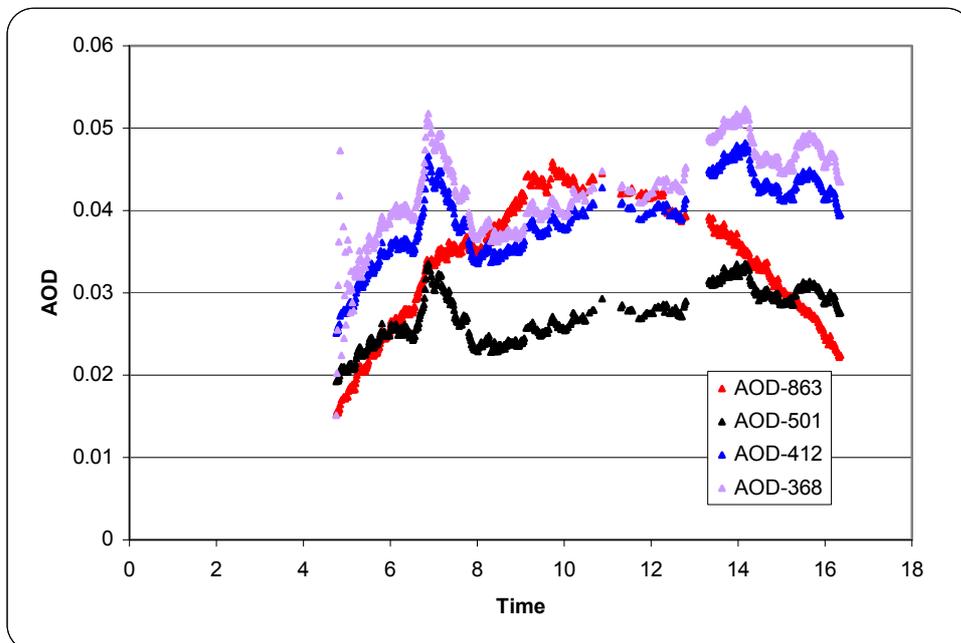


Figure 13: AOD at Ny-Ålesund during the 16<sup>th</sup> September 2002.

The particle sources may be anthropogenic or natural, and trajectories (calculated with the HYSPLIT-model, NOAA) do not give a clear answer to this. Air masses arriving at high

altitude (3000 – 5000 m ) in the morning started 6- 7 days earlier in the northern Pacific and have swept over the Asian continent and Russia, with arrival at Spitsbergen morning/noon when the episode culminated. Analysis of weather maps may be useful for a further assessment of this event. One possible explanation may be the forest fires in Russia in the Moscow region at that time when hundreds of fires in forests and peat bogs caused immense amounts of smoke and problems in the region.

### 3.2 Measurements

Concentration levels for each compound monitored are plotted in Appendix A. Monthly and annual averages are shown in Table 2.

Table 2: Monthly mean concentration levels of climate gases at the Zeppelin station year 2002. All concentrations in pptv, except for methane (ppb), carbon monoxide (ppb), and carbon dioxide (ppm).

Compound	Formula	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
<b>Methane</b>	CH <sub>4</sub>	1850	1852			1798	1786	1781	1785	1809	1824	1821	1831	1813
<b>Carbon monoxide</b>	CO	143	150	149	143	124	94	85	93	120	129	135	148	126
<b>Carbon dioxide*</b>	CO <sub>2</sub>	375	376	377	376	376	372	369			371	372	375	374
<b>Chlorofluorocarbons</b>														
CFC-11	CFCI <sub>3</sub>	267	268		271	272	271	266	261	262	265	266	263	267
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	556	555		569	571	568	561	560	554	557	570	565	562
CFC-113	CF <sub>3</sub> Cl	82	81		81	83	83	83	81	82	83	82	82	82
CFC-114	CF <sub>2</sub> ClCF <sub>2</sub> Cl	17.7	17.7		18.1	18.1	18.3	18.2	19	18.2	18.3	18.0	18.3	18.2
CFC-115	CF <sub>3</sub> CF <sub>2</sub> Cl	8.4	8.5		8.6	8.6	8.6	8.7	8.6	8.7	8.6	8.5	8.5	8.6
<b>Hydrofluorocarbons</b>														
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	2.48	2.43		2.34	2.33	2.52	2.48	2.44	2.59	2.65	2.80	2.99	2.55
HFC-134a	CF <sub>3</sub> CH <sub>2</sub> F	23.9	24.0		24.7	24.8	25.8	25.8	26.8	27.1	28.2	28.9	29.5	26.3
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	3.1	3.2		3.5	3.6	3.6	3.3	3.1	3.1	3.4	3.7	4.0	3.4
<b>Hydrochlorofluorocarbons</b>														
HCFC-22	CHF <sub>2</sub> Cl	163	164		164	166	168	165	166	167	169	171	171	167
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	1.12	1.08		1.14	1.08	1.12	1.05	0.94	0.99	1.05	1.06	1.08	1.06
HCFC-124	CHFClCF <sub>3</sub>	1.66	1.66		1.70	1.68	1.70	1.66	1.70	1.69	1.68	1.69	1.71	1.69
HCFC-141b	CH <sub>3</sub> CFCl <sub>2</sub>	18.9	19.4		19.5	19.1	19.6	19.2		18.9	19.0	19.0	19.2	19.2
HCFC-142b	CH <sub>3</sub> CF <sub>2</sub> Cl	15.4	15.4		16.1	15.9	15.9	15.6	15.7	15.5	15.7	16.2	16.2	15.8
<b>Halons</b>														
H-1301	CF <sub>3</sub> Br	2.95	2.89		3.05	3.08	3.14	3.24	3.23	3.27	3.32	3.29	3.30	3.16
H-1211	CF <sub>2</sub> ClBr	4.46	4.44						4.51	4.54	4.54	4.56	4.57	4.52
<b>Halogenated compounds</b>														
Methylchloride	CH <sub>3</sub> Cl	572	571		586	570	525	473	472	459	475	511	522	521
Methylbromide	CH <sub>3</sub> Br	10.2	10.7		10.8	9.7	8.9	7.8	10.0	9.1	8.7	8.6	8.7	9.4
Methyl iodide	CH <sub>3</sub> I	0.3	0.6		1.2	1.0	1.0	0.8	1.5	0.7	1.0	0.9	0.9	0.9
Methylendichloride	CH <sub>2</sub> Cl <sub>2</sub>	32.8	35.2		34.7	33.9	31.0	26.7	23.5	22.7	25.5	30.2	34.6	30.1
Chloroform	CHCl <sub>3</sub>	11.3	11.4		10.9	10.5	9.8	10.9	10.8	11.1	11.8	11.9	12.0	11.1
Methylchloroform	CH <sub>3</sub> CCl <sub>3</sub>	31.7	32.0		34.2	33.8	32.5	29.8						32.4
Carbontetrachloride	CCl <sub>4</sub>	94	97		99	98	97	92	90	87	91	93	92	94
Perchloroethylene	C <sub>2</sub> Cl <sub>4</sub>	5.6	5.6		5.3	4.4	4.2	3.3	2.5	2.5	3.0	4.5	5.2	4.2
Sulphurhexafluoride	SF <sub>6</sub>	5.2	5.2		5.1	5.1	5.1	5.0	4.9	4.9	4.9	5.0	5.0	5.0

\*Measurements of CO<sub>2</sub> performed by MISU.

#### 4. 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 14 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 by emissions recently, reflecting a global average background level. As HFC-125 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.

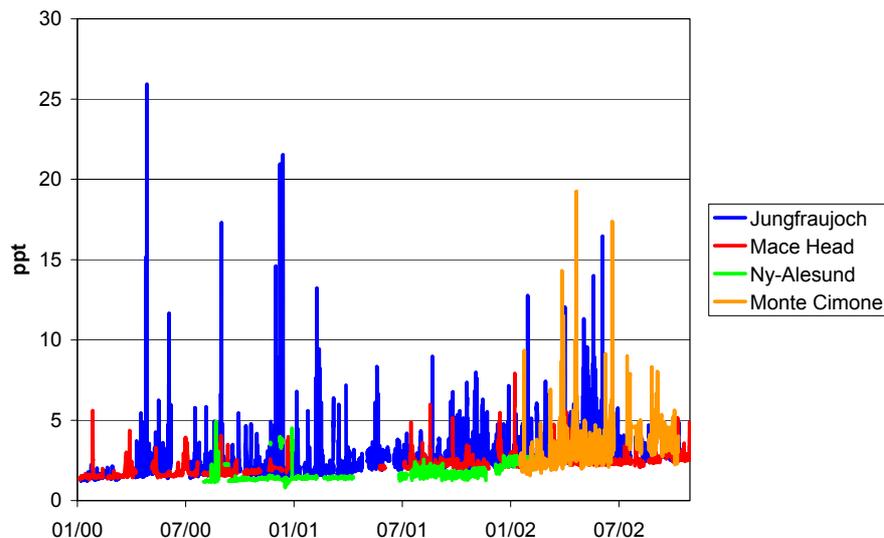


Figure 14: Data series of HFC-125 at four observational sites in the European SOGE network.

In general and in principal, results as depicted in Figure 14 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.

## 4.1 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<sub>6</sub>, PFC, most HFCs and N<sub>2</sub>O such losses can usually be neglected as they are very slow and take place at high levels in the atmosphere. CH<sub>4</sub> 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<sub>2</sub>, 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<sub>6</sub>, PFC and HFCs) that only have anthropogenic emissions that are covered by the Kyoto Protocol. CH<sub>4</sub> and N<sub>2</sub>O, however have significant natural sources that sometimes should not be considered in the Kyoto Protocol. Again, CO<sub>2</sub> 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.

## 4.2 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<sub>2</sub>, 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<sub>6</sub> (Höhne and Harnisch, 2002). The results are depicted in Figures 15 and 16. 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 into 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<sub>6</sub> (residence time 3200 yr, 0.3% loss over 10 yr).

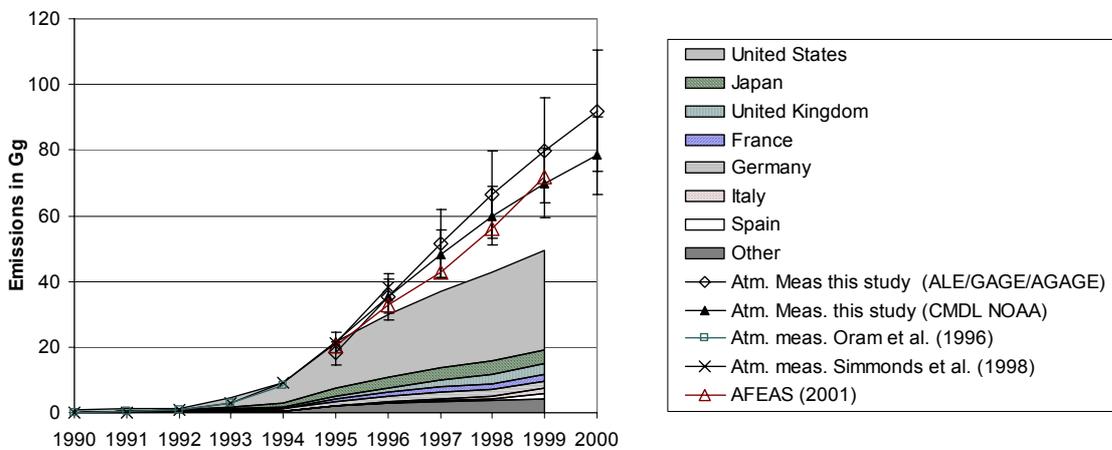


Figure 15: Emission estimates of HFC-134a (Höhne and Harnisch, 2002).

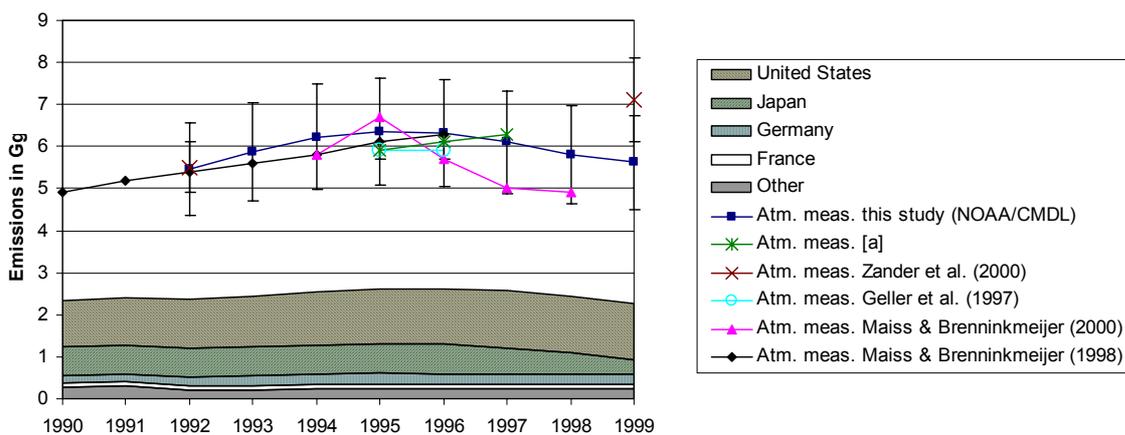


Figure 16: Emission estimates of SF<sub>6</sub> as estimated by Höhne and Harnisch (2002) (see their paper for references to the various observations upon which the estimated have been based).

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 15 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 15 and references which can be found in Höhne and Harnisch, 2002).

For SF<sub>6</sub>, shown in Figure 16, 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.

### **4.3 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.

#### **4.3.1 Dispersion models**

A very simple approach that was adopted at an early stage in support of the LRTAP Protocol is the wind sector allocation pioneered by Schaug et al., 1987. They allocated sectors to arriving air masses according to their history over the last few days of arrival, by calculating air trajectories from analysed winds. This method has been adopted to study emissions of CH<sub>4</sub> and N<sub>2</sub>O (Derwent et al., 1998a) and several CFCs (Derwent et al., 1998b). In the latter study Montreal Protocol substances were studied. However, the HFCs, PFC and SF<sub>6</sub> can generally be studied in similar ways as CFCs. The two studies were based on observations at Mace Head, Ireland, a location that receives air masses alternating from the Atlantic Ocean and from Europe. By contrasting concentrations of CH<sub>4</sub> and N<sub>2</sub>O originating from Europe to those originating from the sea they derived yearly averaged estimates for European emissions in the 1987-1996 period.

Reimann et al. (2002) brought this trajectory-based approach a step further by allocating concentrations and next emissions not only to a given sector, but rather distributing them

along the entire trajectory path. Using data for a long time period this method allows one to establish a spatial distribution of derived emissions. One example is shown in Figure 17, which is based on observations of HFC-152a at three out of the four stations used in Figure 14. The assumption is that emissions are picked up by the air mass at a constant rate, regardless of its location. This is of course a strong simplification, yielding derived emissions even over the ocean. The method underestimates spatial variations in the true emission field. It was used for several HFCs. A general finding was that Northern Italy with its high population and high degree of industrialisation was seen as an important source region for many of the HFCs measured at the Jungfraujoch station.

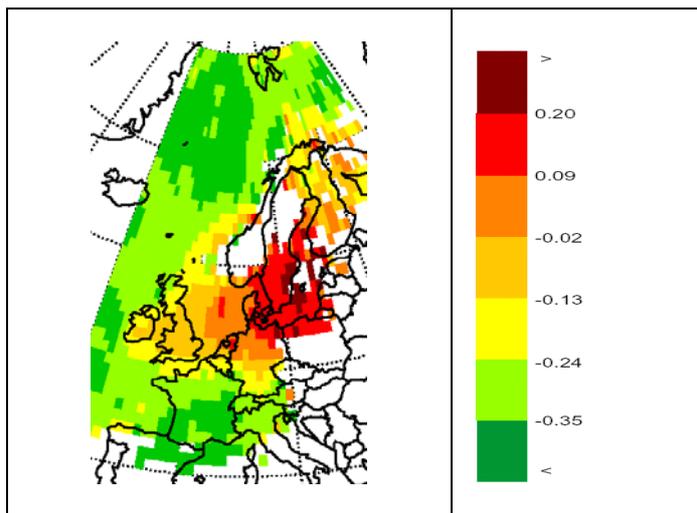


Figure 17: Potential source regions of HFC 152a, allocated by combining the year 2001 measurements at Jungfraujoch, Mace Head and Ny-Ålesund using a statistical trajectory model (values:  $\log(C)$ ). See text for further explanation.

A more comprehensive approach was introduced by Derwent et al. (1998a). They used a dispersion model (NAME) to calculate emissions over a large part of Europe from the continuous observation record of atmospheric measurements at Mace Head, Ireland. The method has been applied to  $\text{CH}_4$  and  $\text{N}_2\text{O}$  (Derwent et al., 1998a) as well as the HFCs 134a and 152a (in addition to a range of Montreal Protocol substances; Derwent et al., 1998b; Ryall et al., 2001). The dispersion model is of a Lagrangian type, in which emissions are modelled by releasing large number of 'particles' into the 'model atmosphere'. The particles are carried along passively by the ambient three-dimensional wind, and also including turbulent diffusion. Each particle represents a mass of released pollutant. All meteorological data, such as wind and temperature fields, are taken from a numerical weather prediction model, at six-, three- and one-hour intervals, with horizontal resolution of about 90, 50 and 16 km, respectively. A nested structure is used. The model has successfully been used to simulate dispersion of a wide range of trace gases.

The main aim of the model studies with the dispersion model is to establish the particular sources that contribute to the concentrations at given observational sites, or receptors. In the model particles are labelled with their location and time of origin, so it is possible to identify the various sources that contribute to a defined receptor and quantify their relative contributions. For those compounds for which there are specific data for European use (from the industrial databases), established emission functions were used to calculate European

releases. The values for 1995 to 1999 were then compared to the model derived emissions in Ryall et al. (2001). The results are shown in Figure 18 (including an additional year's estimates), which contains direct comparisons of the pairs of estimates for up to five separate years (including a range of Montreal Protocol gases to increase the number of species and thus improve the analysis). The relationship between the two sets of results is robust; it appears that the version of NAME described in Ryall et al. (2001) shows emissions estimates consistently lower by a factor of about 1.7 than those calculated from use data. This is most likely due to the way in which the model calculates emissions from outlying regions. The factor 1.7 is a measure of the accuracy of this method. Although this may seem poor, it is considered as a good starting point, as the method has a large potential for improvement, especially by including observations from additional stations receiving air masses from regions other than those arriving at Mace head.

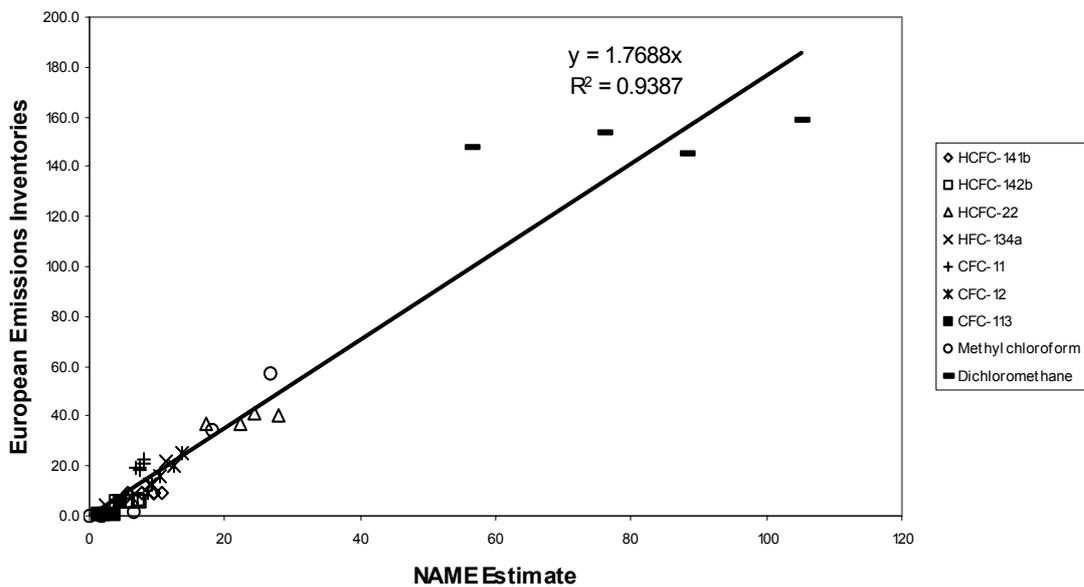


Figure 18: Comparison of estimated European emissions of halocarbons (Gg) by conventional use-plus-emission-function methodology and dispersion modelling by NAME.

A similar method was used by Høst et al. (1999) in studies of SO<sub>2</sub> emissions in Europe. They used a different dispersion model, also starting with emissions derived from. In their comparison between the two sets of emissions they used Bayesian statistics rather than a linear regression (as in Ryall et al., 2001). Another advantage in the analysis of Høst et al. (1999) is the large number of observational sites from which measurements were available. They used 42 stations located over Europe (mainly western, central and northern parts), whereas the Ryall et al. (2001) analysis was based on only one station.

An important implication of the large number of measurement stations is that this allowed a break down of emissions down to the level of individual countries in Europe. As pointed out by Høst et al. (1999) the precision of their method depends on the number and locations of monitoring stations (this is the case for all similar methods). For the Kyoto Protocol substances only a very limited number of stations exist (e.g. 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. As said above, 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.

#### **4.3.2 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 than the methods described previously in this section.

Inverse models have mainly been used to study emissions of CO<sub>2</sub> (e.g. Bousquet et al., 1999a; b; Kaminski et al., 1999a; b), but also CH<sub>4</sub> has been subject of study (e.g. Houweling et al., 1999). Inverse modelling of CO<sub>2</sub> has been successful in estimation of emissions on a continental scale, helping greatly in constraining the total budget of CO<sub>2</sub>. 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<sub>2</sub> in 22 different regions based on altogether 16 different models adopting two different inversion techniques. Although the results quite importantly improve 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<sub>2</sub> 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<sub>2</sub> there is a long way to go before inverse models can be of practical use in the emission work within the UNFCCC.

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## **6. Acknowledgement**

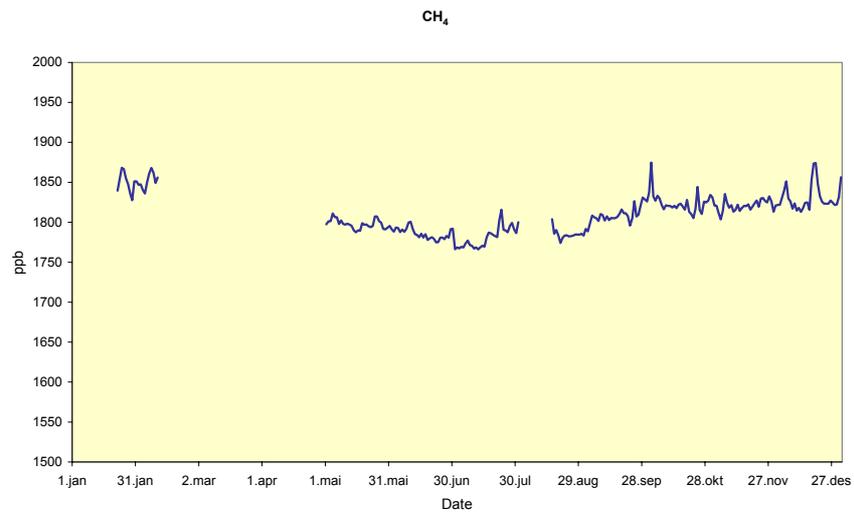
The AOD data from Gotland and Ispra have kindly been provided by Dr. Bertil Hakansson (SMHI) and Dr. Giuseppe Zibordi (JRC, Ispra).

# **Appendix A**

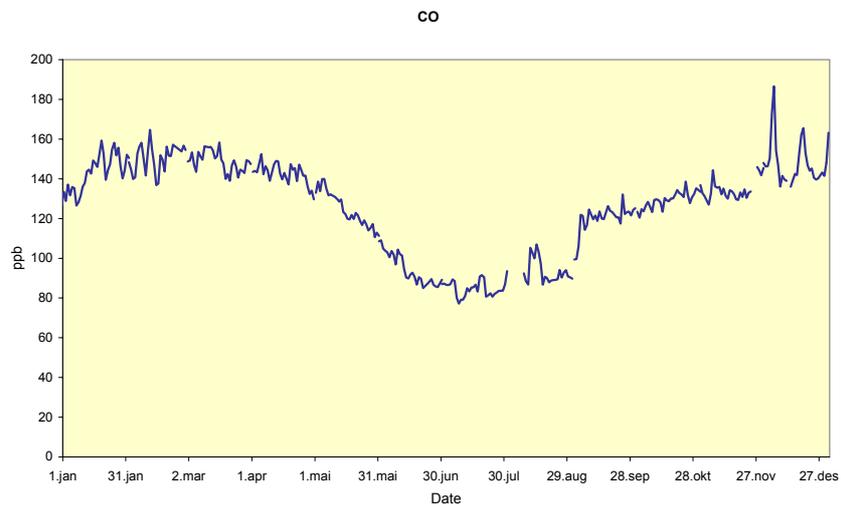
## **Measurement results**



## Methane



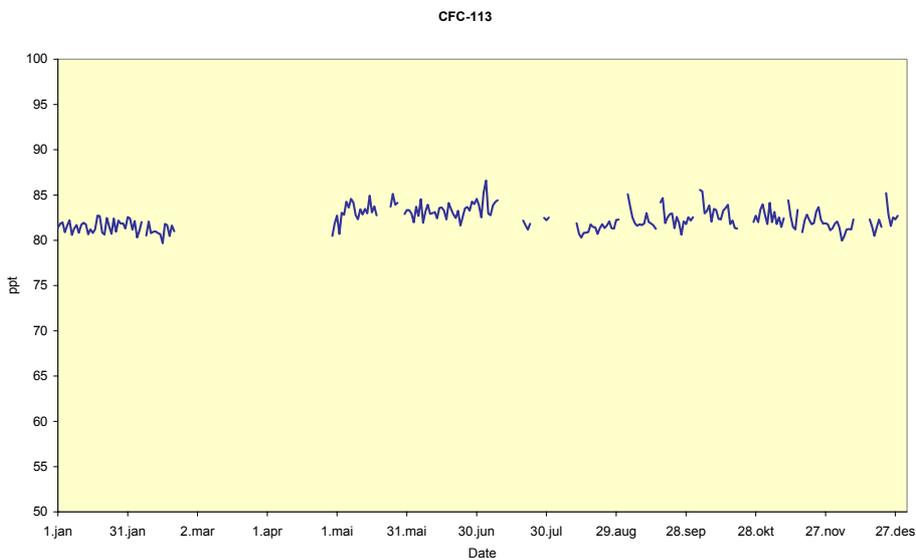
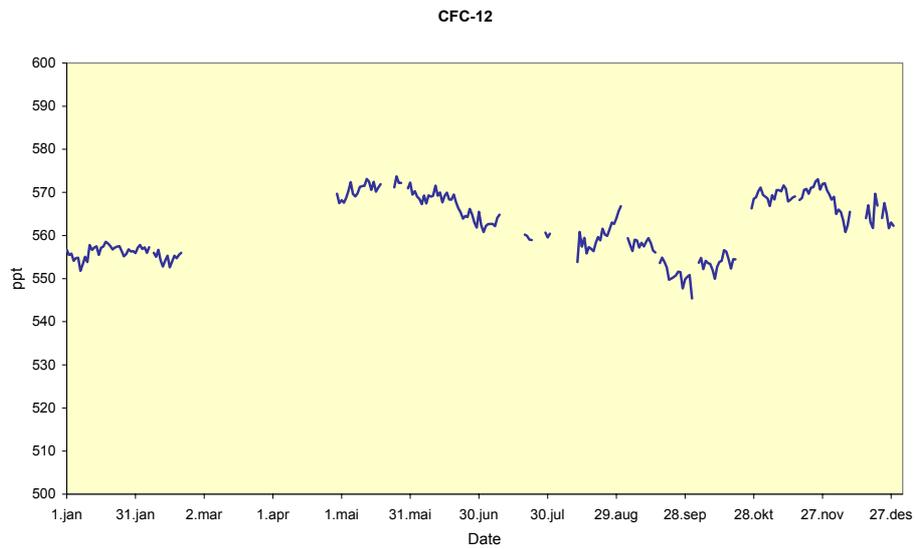
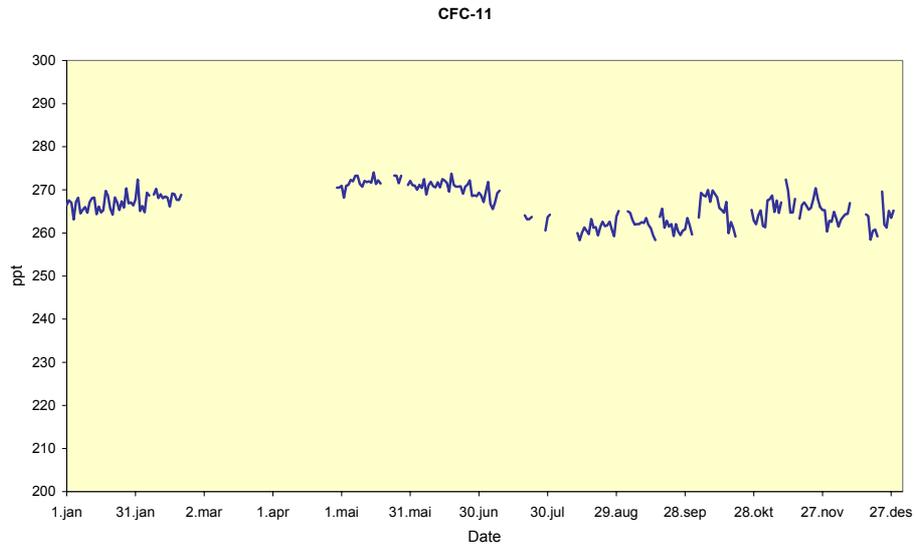
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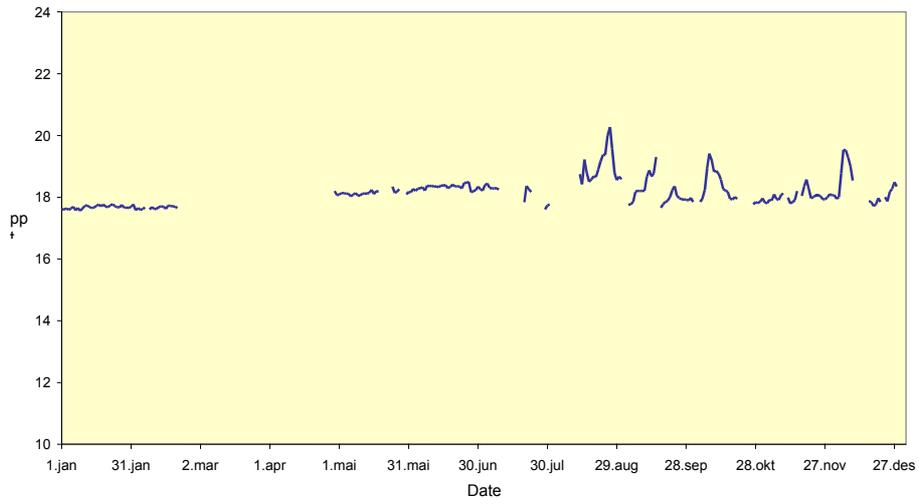
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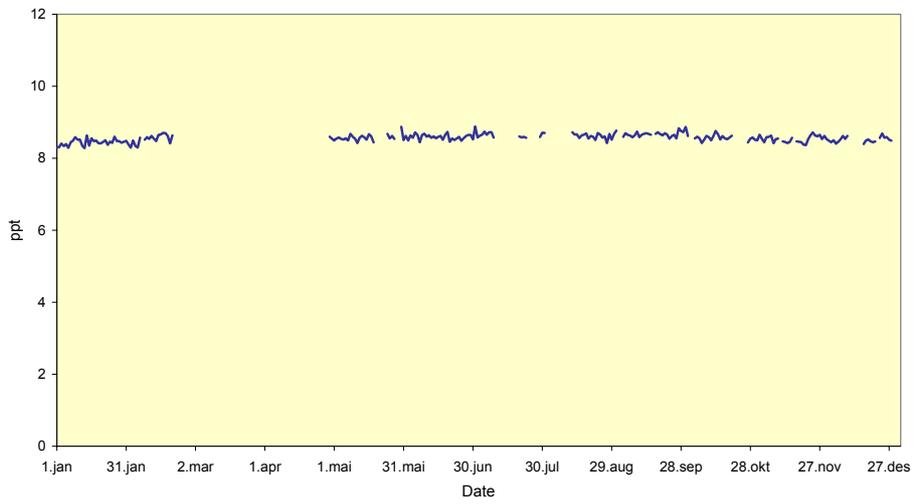
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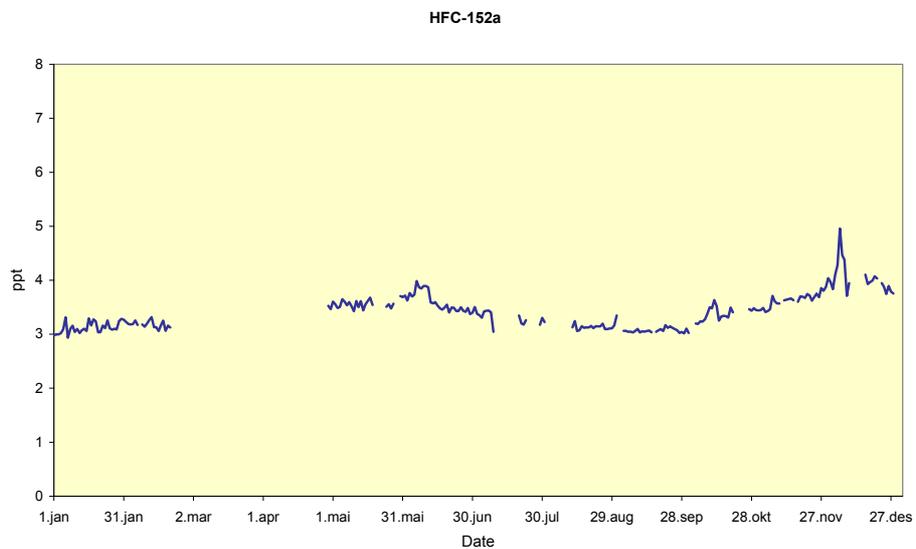
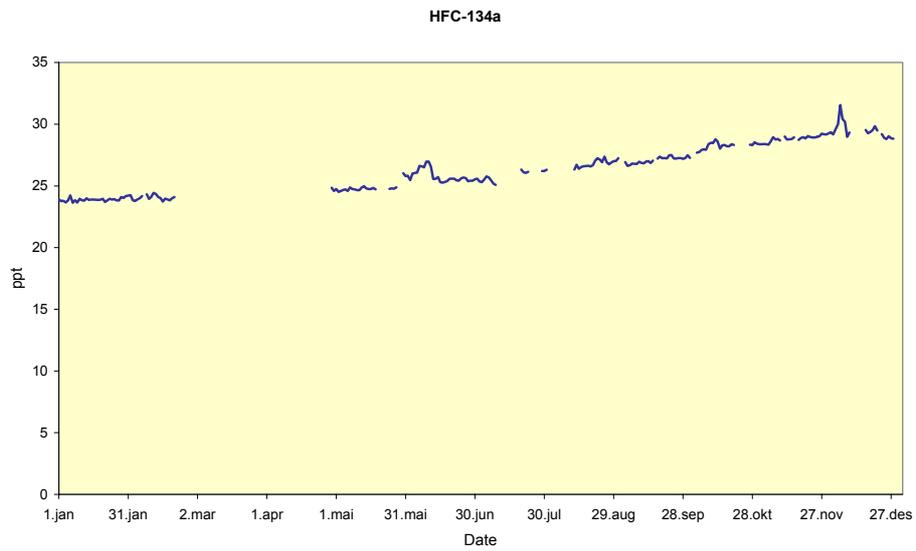
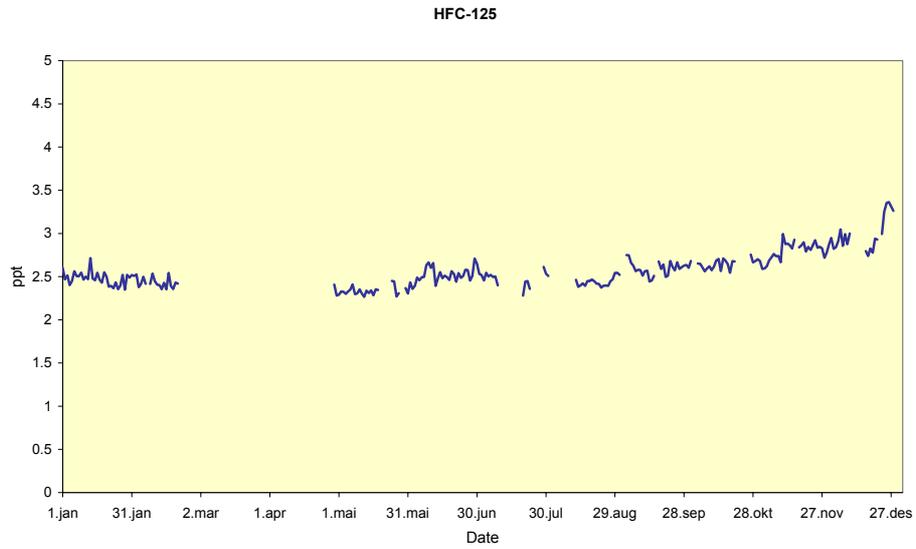
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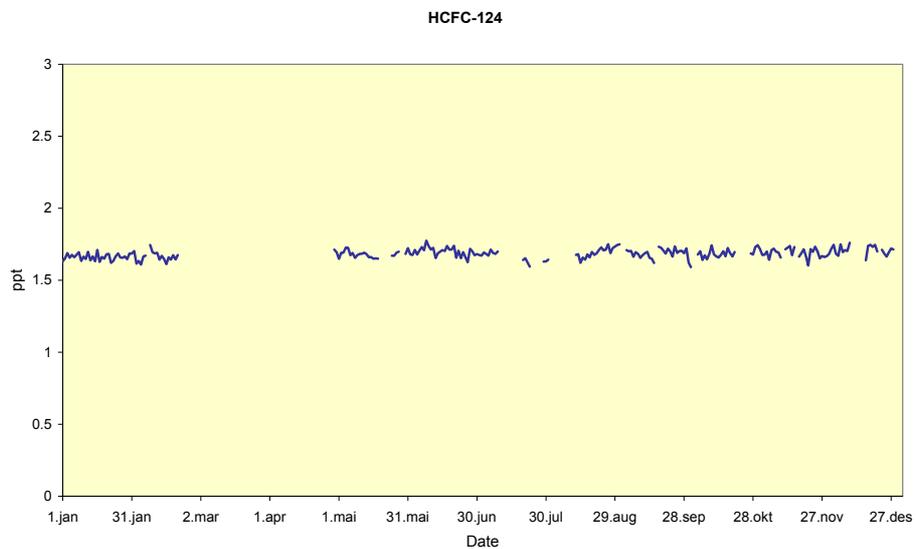
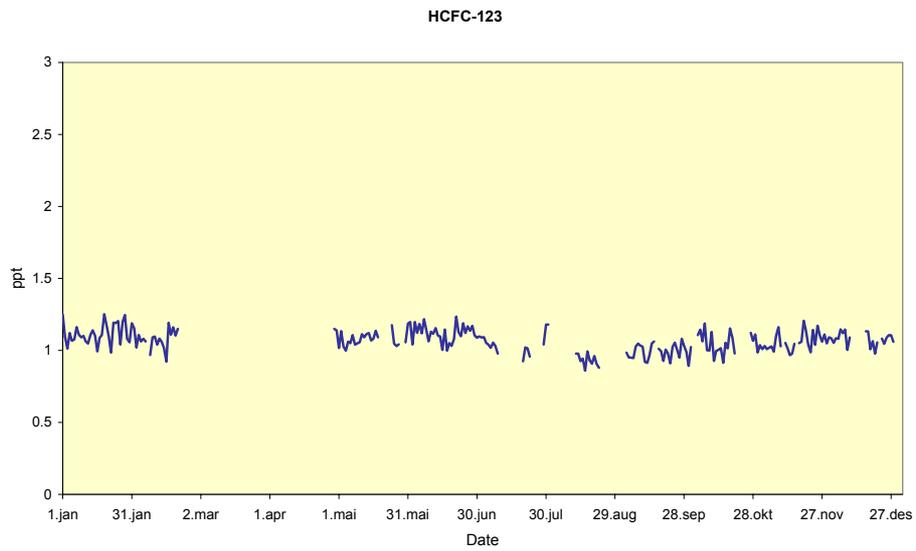
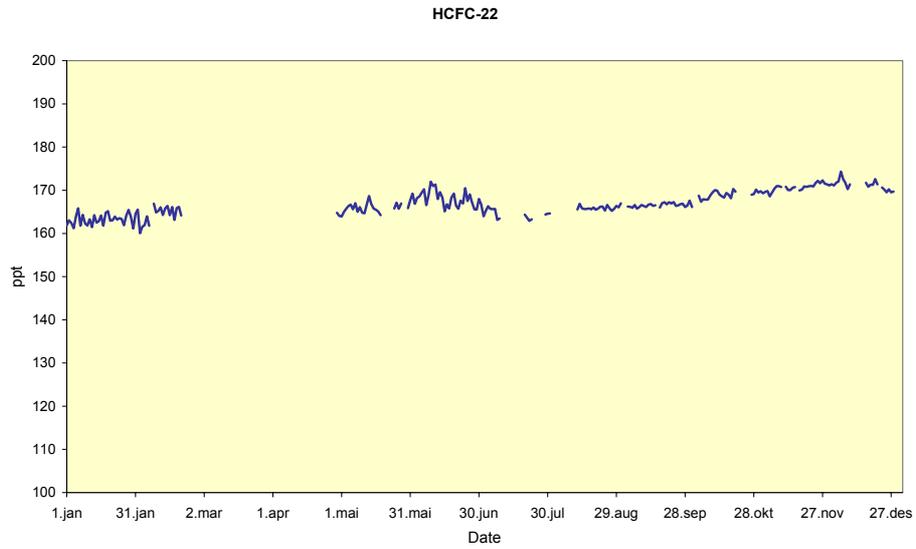
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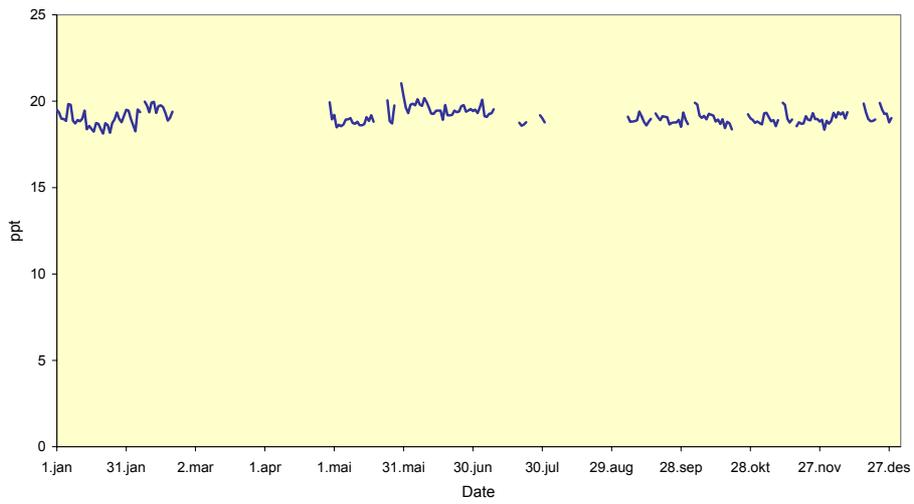
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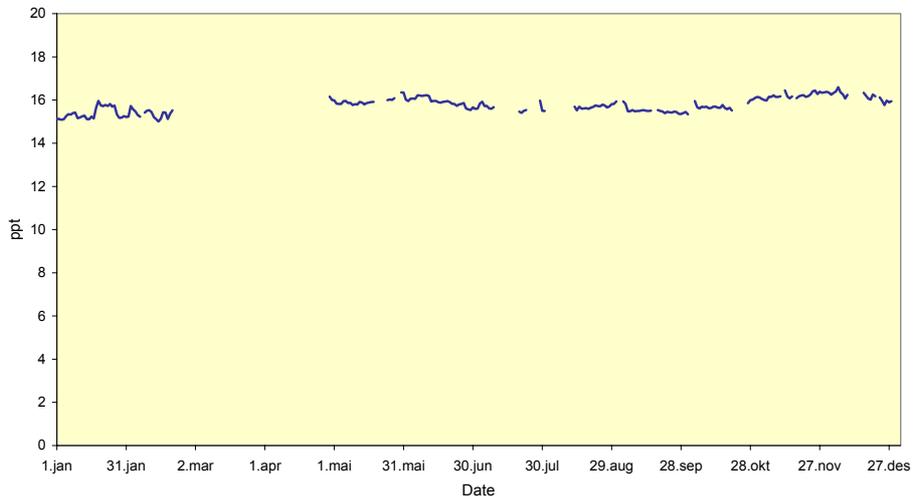
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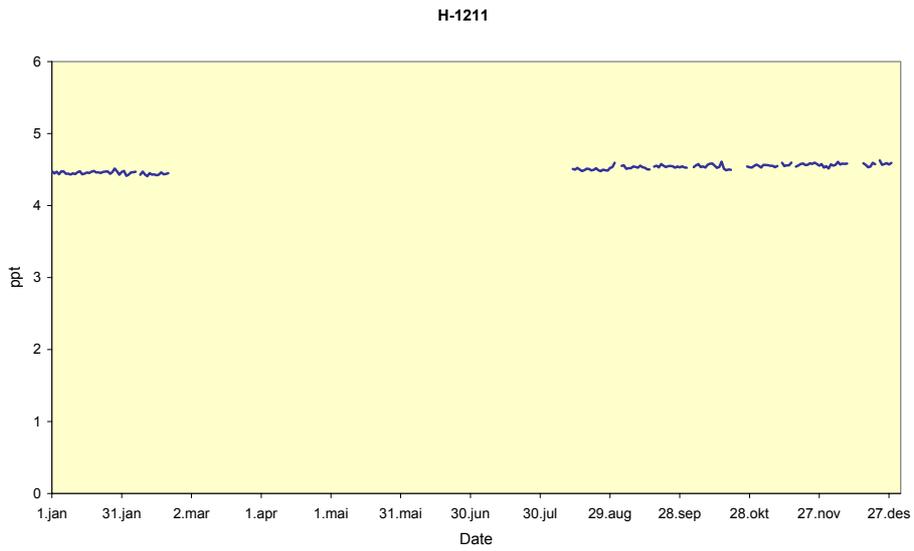
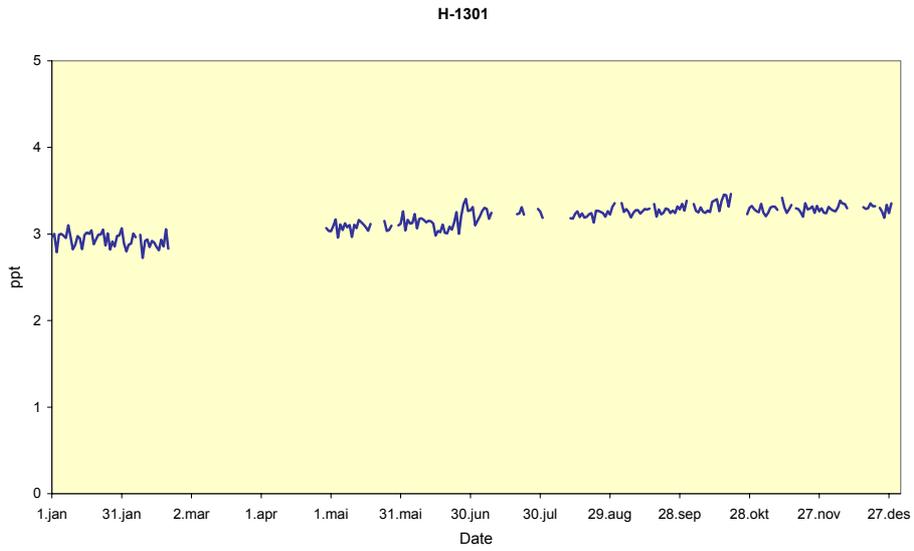
HCFC-141b



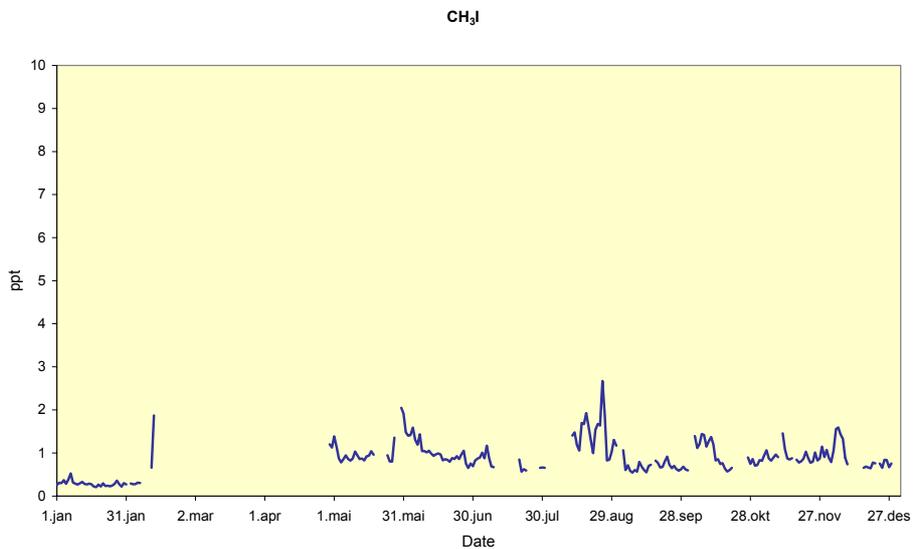
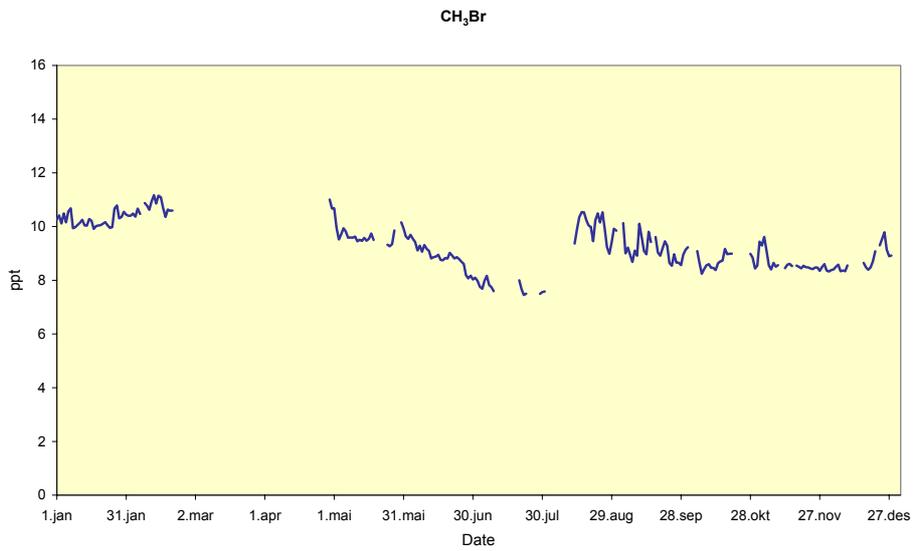
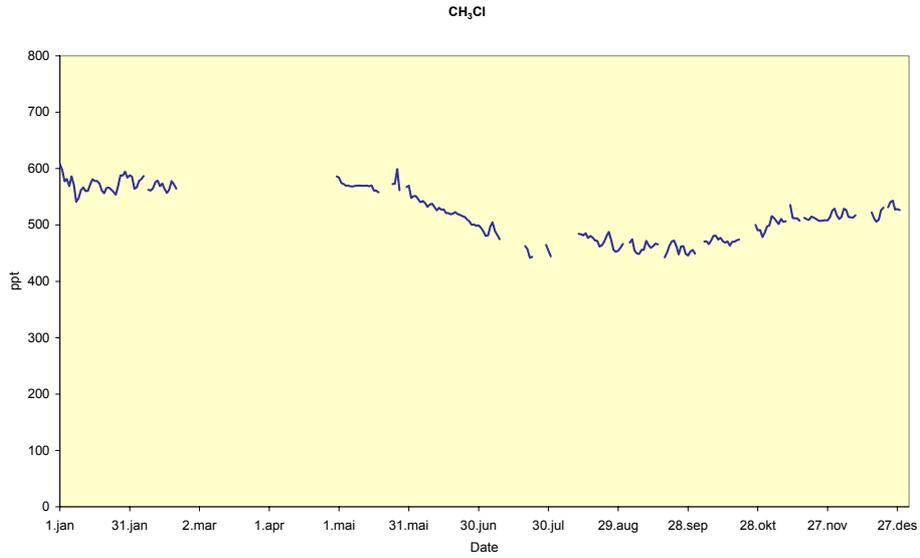
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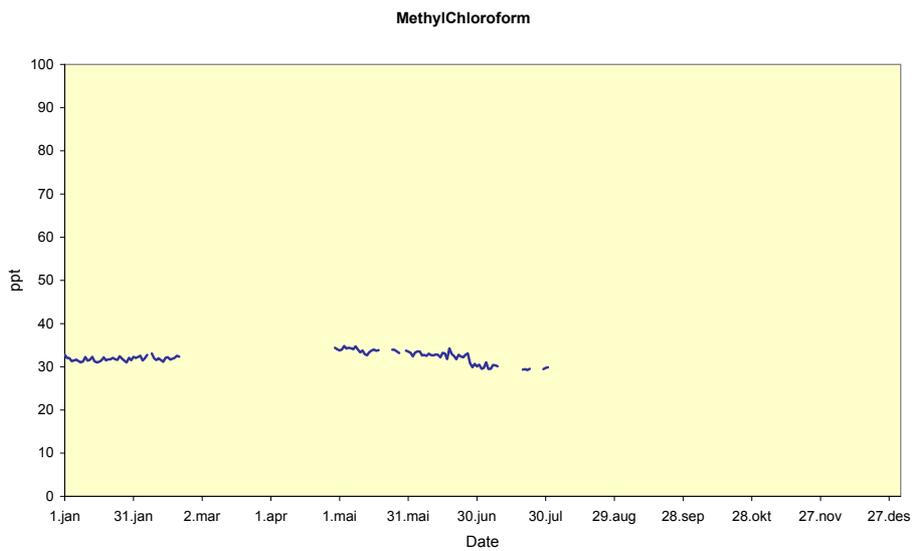
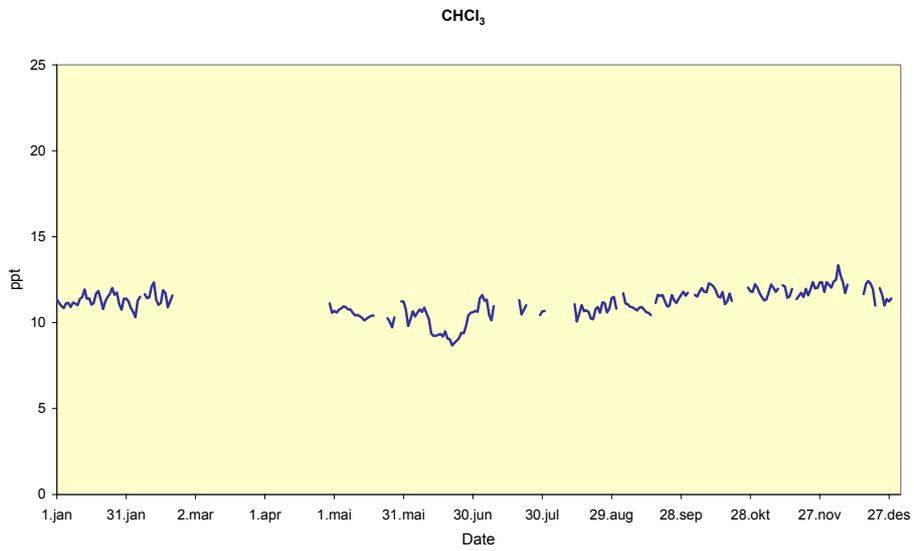
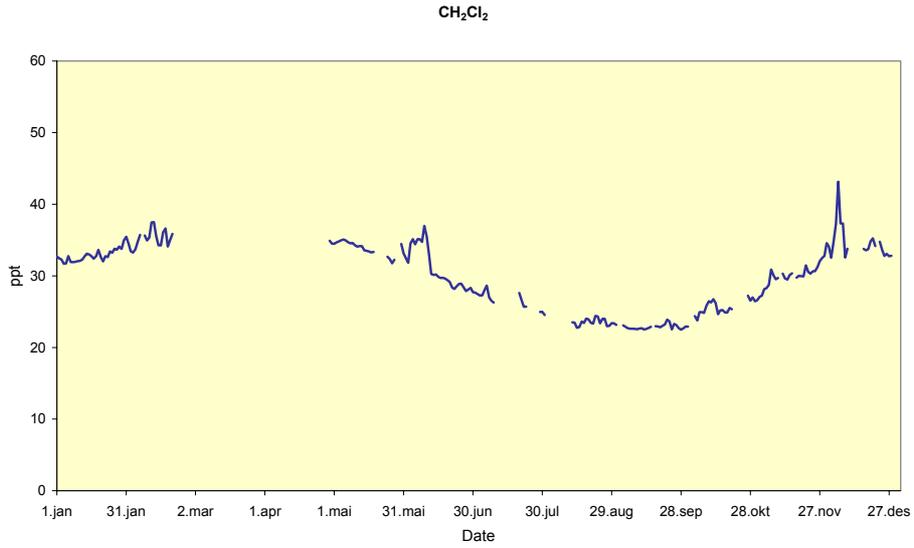


## Halons

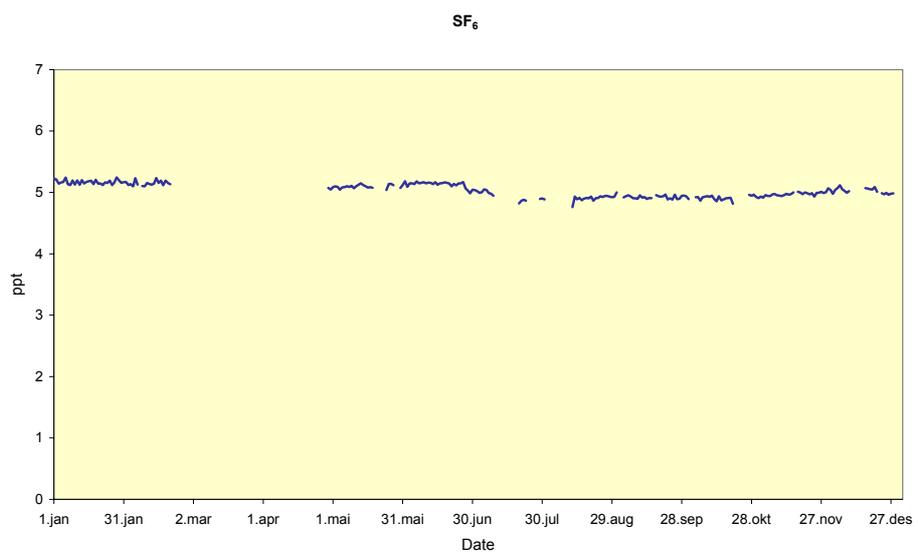
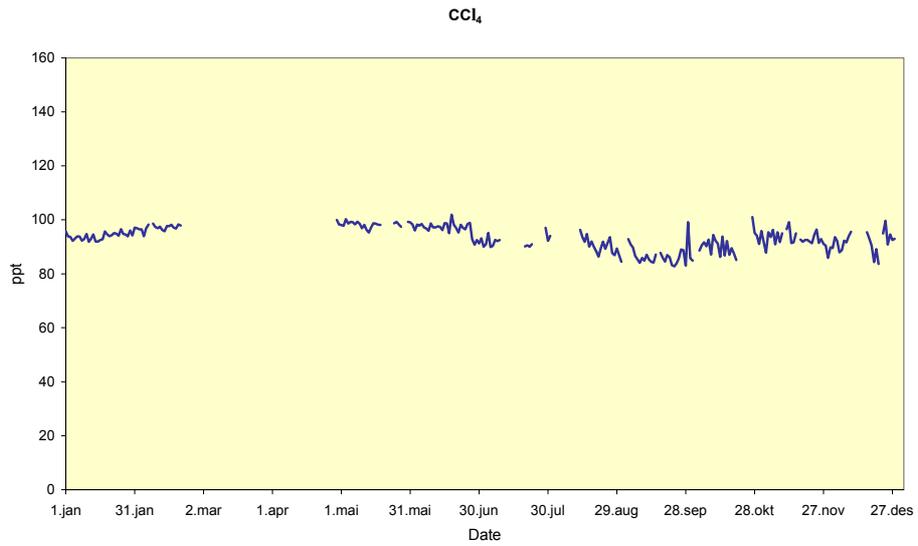


## Other halogenated compounds





Greenhouse gas monitoring at the Zeppelin station - Annual report 2002 (TA-1970/2003)





## Norsk institutt for luftforskning (NILU)

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REPORT SERIES SCIENTIFIC REPORT	REPORT NO. NILU OR 30/2003	ISBN 82-425-1454-2 ISSN 0807-7207	
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		NILU PROJECT NO. O-99093	
AUTHOR(S) O. Hermansen, N. Schmidbauer, C. Lunder, F. Stordal, J. Schaug, O.-A. Braathen (all NILU), K. Holmèn (Department of Meteorology, Stockholm University)		CLASSIFICATION * A	
		CONTRACT REF. M. V. Pettersen, SFT	
REPORT PREPARED FOR Norwegian Pollution Control Authority (SFT) P.O. Box 8100 Dep. NO-0032 OSLO NORWAY			
KEYWORDS Climate	Monitoring		
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 2002. 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 2002			
ABSTRACT (in Norwegian) Rapporten presenterer aktiviteter og måleresultater fra klimagassovervåkingen ved Zeppelinstasjonen på Svalbard i år 2002. Måleprogrammet utføres av Norsk institutt for luftforskning (NILU) og er finansiert av Statens forurensningstilsyn (SFT).			

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- forsuring (sur nedbør)
- ozon (ved bakken og i stratosfæren)
- klimagasser
- miljøgifter

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