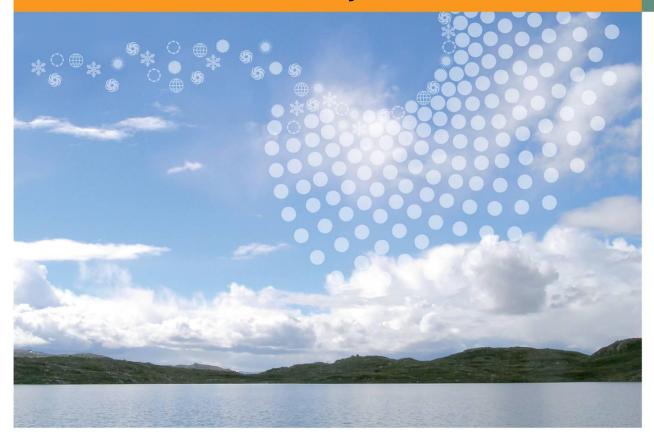


Statlig program for forurensningsovervåking

Annual report 2007

# Greenhouse gas monitoring at the Zeppelin1044station, Svalbard, Norway2009







Statlig program for forurensningsovervåking:

Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway

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# Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway

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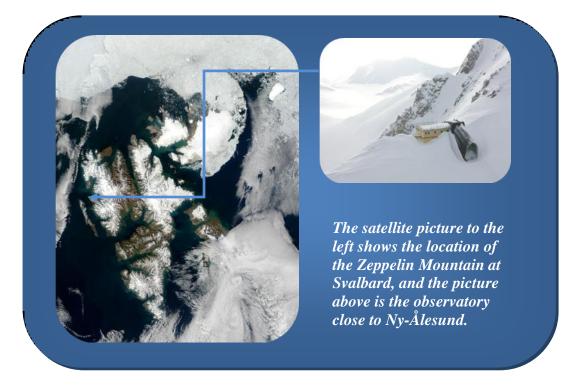
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NILU project no.: O-99093 NILU report no.: OR 02/2009 ISSN 0807-7207 Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway - Annual report 2007 (TA-2480/2009)

# Preface

In 1999 the Norwegian Pollution Control Authority (SFT) and Norwegian Institute for Air research (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 monitoring programme and associated activities, making the Zeppelin observatory a considerable contributor of data on a global as well as a regional scale.

The unique location of the Zeppelin observatory at Svalbard together with the infrastructure of the scientific research community at Ny-Ålesund makes it ideal for monitoring the global changes of the atmosphere. There are few local sources of emissions, and the Arctic location is also important as the Arctic is a particularly vulnerable region.



In 1987 the Montreal Protocol was signed and entered into force in 1989 in order to reduce the production and use of the ozone-depleting substances (ODS). The amount of most ODS in the troposphere is now declining slowly and one expects to be back to pre-1980 levels around year 2050. It is crucial to follow the development of the concentration of these ozone depleting gases in order to verify that the Montreal Protocol and its amendments work as expected. Further these gases and their replacement gases are strong greenhouse gases making it even more important to follow the development of their concentrations.

In December 1997 the Kyoto protocol was adopted. The target set by the Kyoto protocol is to reduce the total emissions of greenhouse gases from the industrialized countries during the period 2008 to 2012. The six most important groups of greenhouse gases included are:  $CO_2$ ,  $CH_4$ ,  $N_2O$ , fluorinated hydrocarbons (HFKs and PFKs) and sulphur hexsafluoride (SF<sub>6</sub>).

This collaborative SFT/NILU programme includes monitoring of 23 greenhouse gases at the Zeppelin observatory in the Arctic. The following are regulated through the Montreal protocol: chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), and halones as well as other halogenated organic gases. Further the following gases included in the Kyoto protocol are monitored; methane (CH<sub>4</sub>), hydrofluorocarbons (HFC), sulphurhexafluoride (SF<sub>6</sub>). Additionally carbon monoxide (CO) and tropospheric ozone (O<sub>3</sub>) are a part of the programme. The amount of particles in the air above the stations is also measured. The station is hosting measurements of carbon dioxide (CO<sub>2</sub>) performed by ITM, University of Stockholm as well. This activity is funded by the Swedish Environmental Protection Agency and the results are included briefly in the report.

The Norwegian Institute for Air Research (NILU) is responsible for the operation and maintenance of the monitoring programme. The purpose of the programme is to:

- Provide continuous measurements of greenhouse gases in the Arctic region resulting in high quality data that can be used in trend analysis
- Provide trend analysis and interpretations
- Provide information on the status and the development of the greenhouse gases with a particular focus on the gases included in the international conventions the Montreal and Kyoto protocol.

Observations and results from the monitoring programme are processed and used to assess the progress towards compliance with international agreements like the Kyoto and the Montreal Protocols. This report summarises the activities and results of the greenhouse gas monitoring programme for the year 2007, and analysis for the period 2001-2007.

Kjeller, January 2009

Cathrine Lund Myhre Senior scientist and Project manager

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Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway - Annual report 2007 (TA-2480/2009)

## 1 Summary

This annual report describes the activities and main results of the programme "Greenhouse gas monitoring at the Zeppelin station in the Norwegian Arctic" for 2007, which is a part of the governmental programme for monitoring pollution in Norway. The report comprises all natural well mixed greenhouse gases (with the exception of  $N_2O$ ), the most important anthropogenic greenhouse gases as well as the amount of particles in the air. Many of the greenhouse gases have also a strong ozone-depleting effect. Table 1 summarises the main results of the observations for the period 2001-2007. The table includes a list with all measured gases, their annual mean values the first and the last year with observations and the trends for the period 2001-2007. Further details and interpretations are presented in section 3.

Table 1: Greenhouse gases measured at Ny-Ålesund together with their trends, lifetimes, and global warming potential (GWP) and their relevance to the Montreal and Kyoto Protocols. The lifetimes and GWPs are updated in accordance with the last IPCC report. All concentrations<sup>1</sup> are in ppt<sub>v</sub>, except for methane and carbon monoxide (ppb<sub>v</sub>) and carbon dioxide (ppm<sub>v</sub>). Trends are calculated for the period 2001-2007 and are given in mixing ratio per year.

Compound	Formula	Life- time (years)	GWP <sup>2</sup>	2001	2007	Trend/ Year	Montreal or Kyoto Protocol	Comments on use for the halocarbons	
Methane	$CH_4$	12.0 <sup>3</sup>	12.0 <sup>3</sup> 23 1857 1877 <b>+2.7 K</b>						
Carbon monoxide	СО			122.5	116.0	-1.1			
Carbondioxide <sup>4</sup>	CO <sub>2</sub>		1	370.9	384.1	+2.3	K		
Chlorofluorocarbons		1							
CFC-11	CCl₃F	45	4600	263	249	-2.29	M phased out	foam blowing, aerosol propellant	
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	100	10600	551	547	-0.71	M phased out	temperature control	
CFC-113		640	6000	82	78	-0.64	M phased out	solvent, electronics industry	
CFC-115	C <sub>2</sub> F <sub>5</sub> Cl	1700	7200	8.3	8.5	+0.03	M phased out	temperature control, aerosol propellant	
Hydrochlorofluoro	carbons								
HCFC-22	CHCIF <sub>2</sub>	11.9	1700	163	199	+6.1	M freeze	temperature control, foam blowing	
HCFC-141b	$C_2H_3FCI_2$	9.3	700	16.8	20.2	+0.6	M freeze	foam blowing, solvent	
HCFC-142b	$CH_3CF_2CI$	19	2400	15.0	19.6	+0.8	M freeze	foam blowing	
Hydrofluorocarbo									
HFC-125	$C_2HF_5$	29	3400	2.03	5.9	+0.7	к	temperature control	
HFC-134a	$CH_2FCF_3$	13.8	1300	20.7	48.3	+4.6	к	temperature control, foam blowing, solvent, aerosol propellent	
HFC-152a	$C_2H_4F_2$	1.4	120	2.8	7.6	+0.8	к	foam blowing	
Halons									
H-1211	$CBrClF_2$	11	1300	4.4	4.5	+0.02	M phased out	fire extinguishing	
H-1301	$CBrF_3$	65	6900	3.0	3.3	+0.05	M phased out	fire extinguishing	
Halogenated comp	Halogenated compounds								
Methylchloride	CH <sub>3</sub> Cl	1.3	16	513	519	+0.96		natural emissions (algae)	
Methylbromide	CH <sub>3</sub> Br	0.7	5	9.1	8.83	-0.05	M freeze	agriculture, natural emissions (algae)	
Dichloromethane	$CH_2Cl_2$	0.5	9	31.1	34.6	+0.6		solvent	
Chloroform	CHCl <sub>3</sub>	0.5	30	10.8	10.5	-0.04		solvent	
Methylchloroform	$C_2H_3Cl_3$	4.8	140	37.8	13.3	-4.1	M phased out	solvent	
Trichloromethane	$C_2HCI_3$			0.5	0.2	-0.05		solvent	
Perchloroethylene	$C_2CI_4$			4.4	2.5	-0.31		solvent	
Sulphurhexafluoride	3200	22200	4.9	6.2	+0.2	К	Mg-production, electronics industry		

<sup>1</sup>The term mixing ratio is commonly used instead of concentrations in atmospheric science. The mixing ratio is the ratio of the number of moles of a constituent in a given volume to the total number of moles of all constituents in that volume. Both annual mean and trends are given in mixing ratio per year.

<sup>2</sup>GWP (Global warming potential) 100 years time period,  $CO_2 = 1$ 

<sup>3</sup> The lifetimes for CH<sub>4</sub> are adjustment times including feedbacks of emission on lifetimes

<sup>4</sup> Measurements of Carbon dioxide is performed by Stockholm University, Department of Applied Environmental Science (ITM)

#### **Greenhouse gases regulated through the Kyoto protocol – Key findings**

The target set by the Kyoto protocol is to reduce the total emissions of greenhouse gases from the industrialized countries during the period 2008 to 2012. This report includes 6 greenhouse gases or groups of gases regulated through the Kyoto protocol. The key findings are:

- Methane  $CH_4$ : The results for the year 2007 show that the mixing ratios of methane have reached new heights with an annual mean value of at 1877 ppb at the Zeppelin observatory. This is an increase of 0.62% since 2006. There is also observed an increase in the methane levels globally from 2006-2007, in average this increase is 0.34 % (WMO, 2008). This is somewhat lower than we have observed at Svalbard which might point towards a possible source at the northern hemisphere, maybe at northern latitudes. The increase at the Zeppelin observatory since 2004 is more than 1% and we consider this as a relatively large change compared to the development of the methane levels in the period from 1999-2005; globally the change was close to zero for this period according to IPCC (Forster et al, 2007), and also at our observatory. Currently there is no explanation for the increase in methane, observed both at Zeppelin and globally. The development and understanding of the levels of this compound have to be followed very carefully the coming years, particularly in the Arctic region, as both permafrost and methane clathrates (so called methane hydrates) in the ocean might be new significant methane emission sources initiated by the observed temperature increase the last years particularly in the Arctic region.
- *Carbon dioxide CO<sub>2</sub>:* The results for the year 2007 show that the mixing ratios of CO<sub>2</sub> have reached new heights at 384.1 ppm. The global mean value for 2007 was 383.1 ppb (WMO, 2008). The annual trend for the period 2001-2007 was +2.3 ppm per year at Zeppelin. The change in CO<sub>2</sub> for the period 2001-2007 has slowed down compared to the period 2001-2006. The observations of CO<sub>2</sub> are performed by the University of Stockholm and are thus only briefly included in the report.
- *Hydrofluorocarbons:* These gases have replaced ozone depleting substances, and are relatively new gases of solely anthropogenic origin. The mixing ratios of HFC-125, HFC-134a, HFC-152a have increased by as much as 190%, 133% and 169% respectively since 2001 at the Zeppelin observatory. We find however that the total radiative forcing for the change in these gases for the period 2001-2007 is only 0.006 W m<sup>-2</sup>. Thus the contribution from these man made gases to the global warming is currently considered small since the concentrations still are very low. It is crucial to follow the development of these gases in the future given the observed rapid increase in concentrations.
- *The perfluorinated compound*  $SF_6$ : The only perfluorinated compound measured at Zeppelin is Sulphurhexacloride, SF<sub>6</sub>. This is an extremely potent greenhouse gas, but the concentration is still very low. However, the concentration has increased by approximately 25% since 2001.

#### **Greenhouse gases regulated through the Montreal protocol – Key findings**

All gases regulated trough the Montreal protocol are substances depleting the ozone layer. In addition they are greenhouse gases. The amount of most of the ozone-depleting substances (ODS) in the troposphere is now declining slowly and one expects to be back to pre-1980 levels around year 2050. In the stratosphere the peak is expected to be reached somewhat later.

The gases included in the monitoring programme are the man-made greenhouse gases called chlorofluorocarbons (CFCs), the hydrogen chlorofluorocarbons (HCFCs), which are CFC substitutes, and halons:

- *CFCs:* In total the development of the CFC gases measured at the global background site Zeppelin should give reason for optimism. The concentrations of the observed CFCs: CFC-11, CFC-12, CFC-113 and CFC-115 are declining. The mixing ratios of three of the four gases have decreased since a maximum level in 2003-2004 and are now at a lower level than in 2001. This is the first year CFC-12 has a negative trend for the investigated period (2001-2007) at Zeppelin. For the compound CFC-115 the growth rate is still positive, but the increase has slowed down and we expect the trend for 2001-2008 to be negative. We find a larger reduction for CFC-11, approximately 2.3 ppt/year, than the global average but for European observations the growth rate for CFC-11 was -2.7 ppt/year for 2003-2004, more in accordance with our results. For CFC-113 the difference with global and European levels is larger. The difference might be explained by the distribution of the sources, and the very remote location of the Zeppelin observatory resulting in a delay of the changes compared to other locations. Further analysis is necessary. The global averaged atmospheric mixing ratio of CFC-12 fits well with our observations.
- *HCFCs:* The CFC substitutes HCFC-22, HCFC-141b and HCFC-142b have all a relatively strong increase in the levels measured at Zeppelin. HCFC-22 used for temperature control and foam blowing has the largest growth rate. This is the most abundant substance of the HCFCs and is currently increasing at a rate of 6.1 ppt/year which is more than 3% per year. HCFC-142b has the strongest relative increase with more than 4% per year.
- *Halons:* The levels of the two gases monitored have been quite stable over the observation period at Zeppelin. However, based on the recent results it seems like there was a maximum in 2004 for halon-1211 at Zeppelin, and a decrease since 2005. According to the last Ozone Assessment (WMO, 2007) it is currently unclear whether the atmospheric mixing ratios of halon-1301 is increasing, but our last observations now indicate that the decline has started in 2006. However this is uncertain, and longer time series are necessary.

#### Greenhouse gases and aerosols not regulated trough the protocols - Key findings

The monitoring programme includes greenhouse gases not regulated through any of the two protocols, and observations of the total amount of aerosols above Ny-Ålesund.

- *Chlorinated greenhouse gases:* These are the following chlorinated gases: Methylchloride (CH<sub>3</sub>Cl), Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), Chloroform (CHCl<sub>3</sub>), Trichloromethane (C<sub>2</sub>HCl<sub>3</sub>), Perchloroethylene (C<sub>2</sub>Cl<sub>4</sub>). The levels of all these gases have decreased the last years except for Dichloromethane. Dichloromethane has had an increase of 11% since 2001.
- *Aerosols:* Observations of the total amount of aerosols above Ny-Ålesund and Zeppelin show increased aerosol levels during the spring. This is as expected and is the so-called Arctic haze which is due to pollution. In 2007 this aerosol pollution was at the same levels as previous years. There are also short episodes later in the year with elevated levels of aerosols, particularly in July and September.

#### Long range transport of pollutions and reactive gases – Key findings

• *Reactive gases:* Tropospheric ozone and CO are compounds with relatively short lifetime in the atmosphere. They are suitable indicators for long range transport of pollution from the continents and biomass burning events. There are several episodes with elevated levels

of ozone and CO in 2007, but none as extreme as in 2006. Based on the CO observations there seems to have been a considerable transport of smoke from biomass burning in March. In general there has been a reduction in CO the last years at Zeppelin, and the annual mean value for 2007 of 116 ppb is the lowest for the period 2001-2007.

• *Long range transport of pollutions:* In 2007 there were relatively few episodes with polluted air transported to Zeppelin, although there was a strong episode in December resulting in record levels of methane. Rather it is important to emphasise the high frequency of days with air categorised as clean air. This means that the observations at Zeppelin were less influenced by long range transport in 2007 than previous years.

## 2 Introduction

The greenhouse effect is a naturally occurring process in the atmosphere caused by trace gases, especially water vapour (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) that naturally occur in the atmosphere. Without these gases the global mean temperature would have been much lower. These gases absorb infrared radiation and thereby trap energy emitted by the Earth. Due to this energy trapping the global mean temperature has increased by more than 30 degrees to approximately 13.7°C (IPCC, 2007). This is the natural greenhouse effect. The enhanced greenhouse effect refers to the additional effect of the greenhouse gases in the atmosphere has increased significantly. The global atmospheric mean mixing ratios of CO<sub>2</sub> has increased by 37% (from 280 ppm as a pre-industrial concentration to 383.1 ppm in 2007) and methane has increased by as much as 156% from 700 ppb to 1789 ppb in 2007) according to WMO (WMO, 2008). These changes in concentrations are the main cause of the global mean temperature rise of 0.74°C over the last century. According to the various IPCC scenarios the temperature will continue to increase with 1.1-6.4°C approaching the year 2100.

Radiative forcing<sup>1</sup> is a useful tool to estimate the relative climate impacts of various components inducing atmospheric radiative changes. The influence of external factors on the climate can be broadly compared using this concept. Revised global-average radiative forcing estimates from the 4<sup>th</sup> IPCC are shown in Figure 1 (IPCC, 2007). The estimates represent radiative forcing caused by changes in anthropogenic factors since pre-industrial time and up to the year 2005.

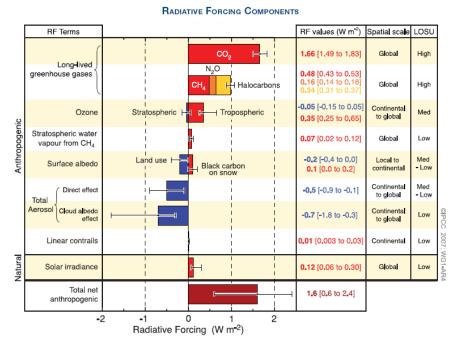


Figure 1: Global-average radiative forcing (RF) estimates for important anthropogenic agents and mechanisms together with the typical spatial scale of the forcing and the assessed level of scientific understanding (LOSU).

<sup>&</sup>lt;sup>1</sup> Radiative forcing is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere. It is an index of the importance of the factor as a potential climate change mechanism. It is expressed in Wm<sup>-2</sup> and positive radiative forcing tends to warm the surface. A negative forcing tends to cool the surface.

The most important greenhouse gas emitted from anthropogenic activities is  $CO_2$  with a radiative forcing of 1.66 W m<sup>-2</sup>. This is an increase of 0.2 W m<sup>-2</sup> since the IPCC report from 2001. CH<sub>4</sub> and N<sub>2</sub>O are other components with strong forcings of 0.48 W m<sup>-2</sup> and 0.16 W m<sup>-2</sup>, respectively. It is worth noting that even the change in  $CO_2$  radiative forcing since 2001 is stronger than the forcing of e.g. N<sub>2</sub>O emphasising the importance of  $CO_2$ .

The joint group of halocarbons is also a significant contributor to the radiative forcing. Halocarbons include a wide range of components. The most important ones are the ozone depleting gases regulated through the Montreal protocol. This includes the CFCs, the HCFCs, chlorocarbons, bromocarbons and halons. Other gases are the HFC (fluorinated halocarbons), PFCs (per fluorinated halocarbons), and SF<sub>6</sub>. These fluorinated gases are regulated through the Kyoto protocol. The total forcing of the halocarbons is 0.337 Wm<sup>-2</sup>, and the single component CFC-12 is presently stronger than N<sub>2</sub>O, but the concentration of CFC-12 seems to have reached its peak value. The trend for CFC-12, seemingly to lower concentrations, gives reason for optimism for this substance. Observations of the halocarbons and methane are central activities at the Zeppelin observatory. Most of the halocarbons have now a negative trend in the development of the atmospheric mixing ratios.

The diagram below shows the relative contribution (in percent) of the long-lived greenhouse gases and ozone to the anthropogenic greenhouse warming sine pre-industrial times (1750). The numbers are based on the radiative forcing estimates in the last IPCC report. The diagram shows that  $CO_2$  has contributed to 55% of the changes in the radiative balance while methane has contributed 16% since pre-industrial times. The halocarbons have contributed 11% to the direct radiative forcing of all long-lived greenhouse gases.

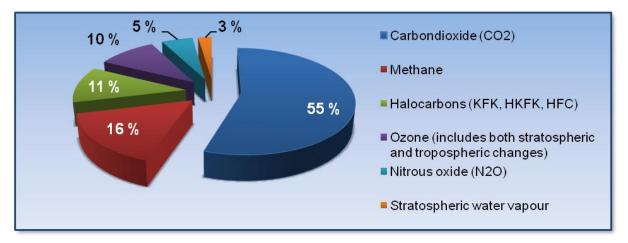


Figure 2: The relative contribution in percent of the long-lived greenhouse gases and ozone to the anthropogenic warming since pre-industrial times (1750). The numbers are based on the radiative forcing estimates in the last IPCC report.

The main objective of NILU's monitoring programme on Svalbard is to observe, analyse and interpret the changes in the gases included on the Montreal protocol and the Kyoto protocol. An overview of all gases observed together with their trends, lifetime and GWP is given in Table 1 in the Summary.

#### The Montreal and the Kyoto protocols

The international collaboration regarding the protection of the ozone layer leading to the Montreal protocol started with the Vienna convention in 1985. Two years later the Montreal

protocol was signed and for the first time there was and international agreement forcing the participating countries to reduce and phase out anthropogenic substances. Halocarbons and their relation to the Montreal protocol are indicated in Table 1.

Today more than 190 countries have ratified the protocol and many countries have also ratified the later additions to the protocol. The Montreal protocol has goals and strategies for all of the ozone reducing substances and the protocol is a part of the UN environmental program UNEP. According to the last ozone assessment report from WMO (WMO, 2007) the total combined abundance of anthropogenic ozone-depleting gases in the troposphere had decreased by 8-9% from the peak value observed in the 1992-1994 time period. This was related to 2005 mixing ratios, and the gases have continued to decrease since.

The target set by the Kyoto protocol is to reduce the total emissions of greenhouse gases from the industrialized countries during the period 2008 to 2012. The four most important greenhouse gases and two groups of gases are included:  $CO_2$ ,  $CH_4$ ,  $N_2O$ , fluorinated hydrocarbons (CFCs and PFCs) and sulphur hexafluoride (SF<sub>6</sub>). The emissions are calculated as annual mean values during the period 2008-2012. The gases are considered jointly and weighted in accordance with their global warming potentials as given by IPCC (2007) and shown in Table 1.

A Norwegian introduction to the Montreal and Kyoto protocol can be found at "Miljøstatus Norge" (http://www.miljostatus.no). The English link to the Montreal protocol is http://ozone.unep.org/Ratification\_status/montreal\_protocol.shtml whereas the Kyoto protocol can be found at http://unfccc.int/essential\_background/kyoto\_protocol/items/1678.php.

A brief introduction is also included in Appendix II in this report.

# **3** Observations and trends of greenhouse gases observed at the Zeppelin station in the Norwegian Arctic

NILU measures 23 greenhouse gases at the Zeppelin observatory at Svalbard. The results from the measurements, analysis and interpretations are presented in this chapter. Also observations and results of CO<sub>2</sub>, which are performed by the Stockholm University – Department of Applied Environmental Science (ITM), are included in the report.

Table 2 presents the main results with annual mean values since the beginning of the observation period in 2001. Also trend per year and change (acceleration) in trend for each component is given. The acceleration in the trend indicates how the growth rate is expected to change in the coming years<sup>2</sup>. Note that all peak concentrations of the measured gases are significantly lower at Ny-Ålesund than at other sites, due to the stations remote location.

Table 2: Yearly average concentration levels of greenhouse gases measured at the Zeppelin station for the years 2001-2007. All concentrations are in  $ppt_v$ , except for methane and carbon monoxide  $(ppb_v)$  and  $CO_2$   $(ppm_v)$ . Trends are calculated from observations for the period 2001-2007.

Compound	Formula	2001	2002	2003	2004	2005	2006	2007	Trend/ year	Change in trend
Methane	CH <sub>4</sub>	1857	1852	1870	1858	1863	1865	1877	+2.7	+1.2
Carbon monoxide	CO	123	130	134	135	132	126	116	-1.1	-3.54
Carbondioxide*	CO <sub>2</sub>	371	373	376	378	381	382	384	+ 2.3	-0.29
Chlorofluorocarbor										
CFC-11	CFCl₃	263	264	263	262	259	255	249	-2.29	-1.28
CFC-12	$CF_2CI_2$	551	559	563	564	561	551	547	-0.71	-3.3
CFC-113	$CF_2CICFCI_2$	82	82	82	82	81	80	78	-0.64	-0.45
CFC-115	CF <sub>3</sub> CF <sub>2</sub> CI	8.3	8.5	8.5	8.6	8.6	8.6	8.5	+0.03	-0.04
Hydrochlorofluoroo										
HCFC-22	CHF <sub>2</sub> CI	163	170	177	184	190	195	199	+ 6.1	-0.67
HCFC-141b	CH <sub>3</sub> CFCl <sub>2</sub>	16.8	17.9	18.8	19.4	19.9	20.1	20.2	+ 0.6	-0.21
HCFC-142b	CH <sub>3</sub> CF <sub>2</sub> Cl	15.0	15.6	16.3	17.0	17.8	18.7	19.6	+ 0.8	+0.05
Hydrofluorocarbon										
HFC-125	$CHF_2CF_3$	2.0	2.6	3.1	3.8	4.4	5.2	5.9	+0.7	+4.49
HFC-134a	$CH_2FCF_3$	20.7	26.0	30.9	35.7	40.1	44.3	48.3	+4.6	-0.25
HFC-152a	$CH_3CHF_2$	2.8	3.4	4.1	4.9	5.7	6.6	7.6	+0.8	+0.09
Halons										
H-1301	CF₃Br	3.0	3.1	3.2	3.3	3.3	3.3	3.3	+ 0.05	-0.03
H-1211	CF <sub>2</sub> ClBr	4.4	4.5	4.6	4.7	4.7	4.6	4.5	+ 0.02	-0.05
Halogenated comp										
Methyl Chloride	CH₃CI	513	520	524	526	526	523	519	+0.96	-2.32
Methyl Bromide	CH₃Br	9.1	9.0	8.9	8.8	8.8	8.8	8.8	-0.05	+ 0.03
Dichloromethane	$CH_2CI_2$	31.1	31.3	32.6	32.1	32.8	33.6	34.6	+0.6	+ 0.16
Chloroform	CHCl <sub>3</sub>	10.8	10.7	10.6	10.5	10.5	10.5	10.5	-0.04	+0.02
Trichloromethane	CH <sub>3</sub> CCI <sub>3</sub>	37.8	32.3	27.4	23.1	19.2	16.0	13.3	-4.1	+0.55
TriChloroethylene	CHCICCI <sub>2</sub>	0.5	0.4	0.4	0.3	0.3	0.3	0.2	-0.05	-0.01
Perchloroethylene	$CCI_2CCI_2$	4.4	4.0	3.6	3.2	2.9	2.7	2.5	-0.31	+0.06
Sulphurhexafluoride	SF <sub>6</sub>	4.9	5.1	5.3	5.5	5.8	6.0	6.2	+ 0.2	+0.02

\* Measurements of Carbondioxide performed by Stockholm University, Department of Applied Environmental Science (ITM)

 $<sup>^{2}</sup>$  As the time series still are short and the seasonal and annual variations are large for many of the components, there are considerable uncertainties connected with the results.

Greenhouse gases have numerous sources both anthropogenic and natural. Trends and future changes in concentrations are determined by their sources and the sinks, and in section 3.1 are observations and trends of the monitored greenhouse gases with both natural and anthropogenic sources presented in more detail. In section 3.2 are the detailed results of the gases with purely anthropogenic sources presented. These gases are not only greenhouse gases but also a considerable source of chlorine and bromine in the stratosphere, and are thus responsible for the ozone depletion and the ozone hole discovered in 1984. These gases are controlled and regulated through the successful Montreal protocol. Section 3.3 describes the Zeppelin observatory at Svalbard where the measurements take place and the importance of the unique location. A description of the instrumental and theoretical methods applied is included in Appendix I.

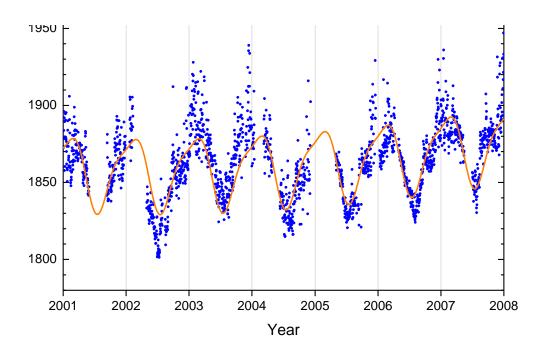
#### 3.1 Greenhouse gases with natural and anthropogenic sources

All gases presented in this section (Methane, Carbon Dioxide, Methyl Chloride, Methyl Bromide, CO and  $O_3$ ) have both natural and anthropogenic sources. This makes it complex to interpret the observed changes as the sources and sinks are numerous. Moreover, several of these gases are produced in the atmosphere from chemical precursor gases and often also dependent on the solar intensity.

#### 3.1.1 Observations of methane in the period 2001-2007

Methane (CH<sub>4</sub>) is the second largest greenhouse gas after CO<sub>2</sub> with a radiative forcing of 0.48 W m<sup>-2</sup> since 1750. In addition to be a crucial greenhouse gas, methane also plays a significant role in the atmospheric chemistry. Methane is destroyed by the reaction with the hydroxyl radical (OH) giving water vapour. The OH radical has a crucial role in the tropospheric chemistry by reactions with many emitted components and thus are responsible of the cleaning of the atmosphere. Increased levels of methane might lower the concentration of OH. Furthermore methane is important for the ozone layer chemistry by being an important source of bringing water vapour to the stratosphere (*Forster et al.*, 2007).

The atmospheric methane concentration has been relatively stable the last 10 years, both globally and at Zeppelin observatory since 2001 when the measurements started. 2003 was an exception; a maximum annual mean of 1870 ppb at Zeppelin was obtained, considerable higher that the other years. This was also the previous record year globally. Recently an increase in the methane levels is evident from our observations, and also observations at other sites. Figure 3 presents the observations of methane at Zeppelin since the start in 2001.



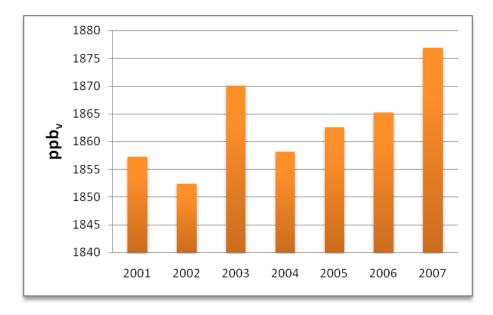
*Figure 3: Observations of methane for the period 2001-2007 at the Zeppelin observatory. Blue dots: observations, orange solid line: modelled background methane concentrations.* 

As can be seen there is an increase in the concentrations of methane observed at Zeppelin the last years and particularly in 2007. The pronounced increase started in November/December 2006 and continues throughout the year 2007, and is particularly evident in the late summerwinter 2007. The maximum methane mixing ratio was detected 10<sup>th</sup> December and was as high as 1956 ppb. This seems to be the highest value ever recorded at Zeppelin. Analysis of source regions is included in section 5 on page 40.

To retrieve the annual trends in the methane levels for the entire period the observations have been fitted by an empirical equation as described in Appendix I. The modelled methane values are included as the orange solid line in the Figure. Only the observations resulting from clean air arriving at Zeppelin are used in the model, thus the model represents the background level of methane at the site.

The average annual growth rate is  $+2.7 \text{ ppb}_v$  per year for the period 2001-2007 this corresponds to an increase of 0.14% per year. Comparably the annual trend for the period 2001-2006 was  $+1.9 \text{ ppb}_v$  thus the last year's increase has changed this by more than 40%. The acceleration in the trend is positive, 1.2, (see Table 2) indicating that the growth rate year is expected to increase in the coming years. Although, this is connected with large uncertainty as the reason for the observed increase is not clear. (Additionally, the seasonal and annual variations are large and the time series are still short.)

The increase in the methane levels the last years is better visualized in Figure 4 showing the  $CH_4$  annual mean mixing ratio for the period 2001-2007. The annual means are based on a combination of the observed methane values and the modelled background values; during periods with lacking observations we have used the modelled background mixing ratios in the calculation of the annual mean.



*Figure 4: Development of the annual mean mixing ratio of methane measured at the Zeppelin Observatory for the period 2001-2007.* 

This diagram clearly illustrates the large increase in the concentrations of methane in 2007 starting already in 2006 as shown in Figure 3. All annual means are included in Table 2 on page 14. The annual mean mixing ratio for 2007 was 1877 ppb<sub>v</sub> while the level was 1865 ppb<sub>v</sub> in 2006. This is an increase of 0.62%. The increase since 2004 is more than 1% which is considered as relatively large compared to the development of the methane mixing ratio in the period from 1999-2005. The global average change was close to zero for this period according to IPCC (Forster et al, 2007), and also at our site until 2005.

Also stations at other locations show a significant increase in methane for the year 2007, at both hemispheres. The global annual mean concentration reported by IPCC for the year 2005 was 1774 ppb<sub>v</sub> (IPCC, 2007). According to WMO (WMO, 2008) there has been a global increase in the methane concentration from 1782 ppb in 2006 to 1789 ppb in 2007 (0.34%). Rigby and his co-workers report a global increase of methane in a recent article in the Geophysical Research Letters (Rigby et al, 2008). They have analyzed methane data from 12 sites worldwide, and found an increase of around 10 ppb<sub>v</sub> at all sites. The largest increase was observed at Mace Head in Ireland and Alert. Alert is a site north in Canada (82 °N), and the site closest to the Zeppelin observatory at Svalbard.

The reason for the large increase observed is unclear, although several hypotheses are raised. It is now crucial to try to understand and explain the observed increase. To do this we need to analyse the possible recent changes in the sources and sinks in methane.

The average  $CH_4$  concentration in the atmosphere is determined by a balance between emission from the various sources at the surface and destruction by free hydroxyl radicals (OH) in the troposphere. In the stratosphere  $CH_4$  is destroyed by short wave radiation. The atmospheric lifetime of methane is 12 years (Forster et al, 2007).

The main sources of methane today include boreal and tropical wetlands (including rice paddies), emission from ruminant animals, biomass burning and fossil fuels combustion. Further, methane is the principal component of natural gas. Of natural sources there is a large

unknown amount of methane in methane clathrates (so called methane hydrates) in the ocean floors. Other sources include mud volcanoes which are connected with deep geological faults, and also emissions from plants are suggested (Keppler et al., 2006). Further a large unknown amount of methane is bounded in the permafrost layer in Siberia and North America and this might be released if the permafrost layer melts as a feed back to climate change. According to the last IPCC report (Alley et al., 2007) the temperature of the top of the permafrost layer has generally increased by up to  $3^{\circ}$ C since 1980s.

Currently the observed increase is not explained or understood. According to Rigby et al. (2008) there might be signs of a reduction in the hydroxyl radical OH, which is essential in the destruction of methane, but this is not in agreement with other observations. Furthermore, the OH concentration is low in the Arctic particularly during autumn and winter. There might also be new sources. High effort should be put on the issue to explain the increase in the  $CH_4$  concentrations as the consequence might be severe. The high levels observed in 2003 are also a global feature, and i still not understood. It is essential to find out if the increase is due to large one-time point emission, or of it is new initiated process releasing methane to the atmosphere as the melting of the permafrost layer. But still it is too early to conclude if the trend will continue in 2008 and 2009.

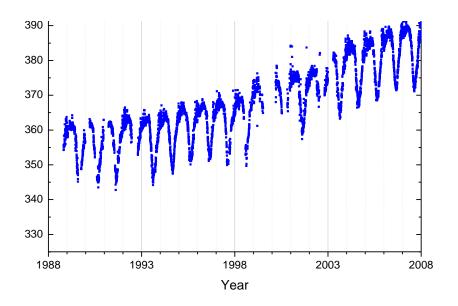
We have performed an analysis and understanding of the source regions of the air arriving at Zeppelin in the period 2001-2007 as described in section 5 at page 40. The most striking of this analysis is that in 2007 are the air arriving at Zeppelin categorized as clean marine and Arctic air as much as 67% of the time compared to around 53 ( $\pm$ 5) % the previous years. This can point in the direction of an Arctic source or accumulation of methane in the Arctic, particularly during late summer and autumn. Also the year 2003 with the second highest methane concentration had a large fraction of clean air arriving at Zeppelin.

We will continue to work on the analysis of the methane levels. As a part of this we will try to assess the contribution from the emissions from regional sources like Melkøya and the flaring at the new LNG (Liquefied Natural Gas) plant in Hammerfest. The emissions of  $CO_2$  from Melkøya in 2007 was more than 1.6 million tons (Statistics Norway, www.ssb.no), and there were also high methane emissions.

#### 3.1.2 Observations of Carbon Dioxide (CO<sub>2</sub>) in the period 1988-2007

 $CO_2$  is the most important greenhouse gases with a radiative forcing of 1.66 W m<sup>-2</sup> since 1750 and an increase in the forcing of as much as 0.2 W m<sup>-2</sup> since the IPCC report from 2001 (Forster et al., 2007).  $CO_2$  is the end product of the destruction of all main organic compounds in the atmosphere and has shown an increase of as much as 37 % since the pre industrial time.

The atmospheric  $CO_2$  concentration measured at Zeppelin Observatory for the period 2001-2007 is presented in Figure 5. This data are provided by ITM University of Stockholm and we acknowledge the effort they are doing in monitoring  $CO_2$  at the site.



*Figure 5: The CO*<sub>2</sub> *concentration measured at Zeppelin Observatory for the period 2001-2007.* 

The results show a continues increase since the start of the observations and in Figure 6 is the development of the annual mean concentrations measured at Zeppelin observatory for the period 1988-2007 shown.

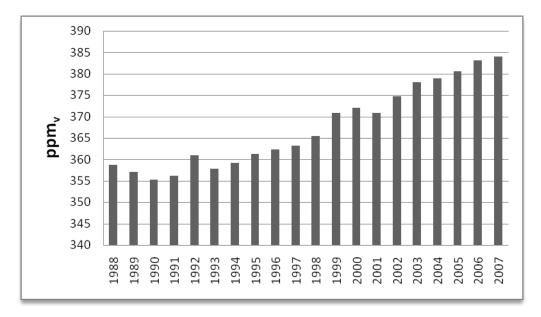


Figure 6: Development of the annual mean mixing ratio of  $CO_2$  measured at Zeppelin observatory for the period 1988-2007.

The results show that 2007 is a new record year for the annual mixing ratio of  $CO_2$  at Zeppelin. The mean value for 2007 was 384.1 ppm. The global mean value for 2007 was 383.1 ppb. The main reason why it is higher at Zeppelin than globally is that in general the  $CO_2$  emissions is lower at the Southern hemisphere and the global mixing takes a certain time.

The annual trend for the period 2001-2007 was +2.3 ppm per year, and the change in trend was slightly negative. This means that the growth rate for the period 2001-2007 has slowed down compared to the period 2001-2006.

A more detailed analysis of this result with comparison to other sites is considered as central and valuable. However, as this component is not included in the national monitoring programme, we are not in a position where we can analyse the data further.

#### 3.1.3 Observations of Methyl Chloride in the period 2001-2007

The main source of Methyl Chloride in the atmosphere is algae in the oceans thus this compound are not regulated trough any of the Montreal or Kyoto protocols. The results of the observation of this substance are shown in Figure 7.

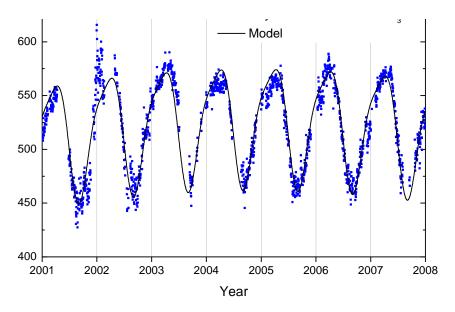


Figure 7: Observations of Methyl Chloride,  $CH_3Cl$ , for the period 2001-2007 at the Zeppelin observatory. Dots: daily averaged concentrations from the observations, solid line: modelled background concentrations.

The lifetime of the compound is only 1.3 year resulting in large seasonal fluctuations as shown in the Figure. The degradation of the compound is dependent on solar intensity. To reach the stratosphere, the lifetime in general needs to be in the order of 2-4 years to have significant chorine contribution. However, Methyl Chlorine has relatively high mixing ratios, and will contribute to the stratospheric Chlorine burden. With respect to the warming potential this substance is 16 times stronger than  $CO_2$  per kg gas.

By use of the model described in Appendix I we have calculated the annual trend, and change in trend also given in Table 2. The trend for the period 2001-2007 is 0.96 ppt per year, and the change in the trend is -2.32. This indicates that the reduction in the mixing ratio of this substance is expected to be relatively large for the coming years and we expect trend to be close to zero for the period 2001-2008 if there are no large abrupt changes in the emissions.

Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway - Annual report 2007 (TA-2480/2009)

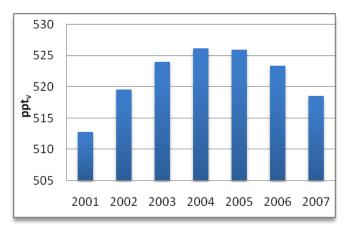


Figure 8: Development of the annual means Methyl Chloride measured at the Zeppelin Observatory for the period 2001-2007

The development of the annual means of Methyl Chloride for the period 2001-2007 is presented in Figure 8. The last years there has been a decrease in the annual means. As the main source of this compound is algae from the ocean, it is interesting to note that the decrease is large from 2006-2007 at Zeppelin despite the fact that this was a year with record low sea ice cover in the Arctic region, and high temperatures.

#### 3.1.4 Observations of Methyl Bromide in the period 2001-2007

The sources of Methyl Bromide ( $CH_3Br$ ) are both from natural and anthropogenic activities. The natural sources such as the ocean, plants, and soil, can also be a sink for this substance. Additionally there are also significant anthropogenic sources; it is used in a broad spectrum of pesticides in the control of pest insects, nematodes, weeds, pathogens, and rodents. It is also used in agriculture primarily for soil fumigation, as well as for commodity and quarantine treatment, and structural fumigation.

The results of the daily averaged observations of this compound for the period 2001-2007 are shown in the Figure below.

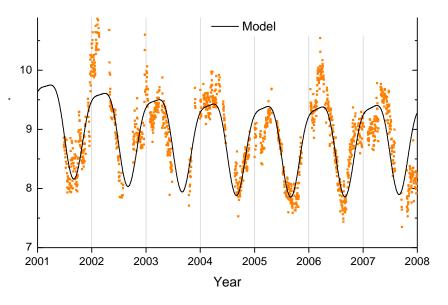


Figure 9: Observations of Methyl Bromide,  $CH_3Br$ , for the period 2001-2007 at the Zeppelin observatory. Dots: daily averages mixing ratios from observations, solid lines: modelled background concentrations.

While methyl bromide is a natural substance, the additional methyl bromide added to the atmosphere by humans contributes to the thinning of the ozone layer. Total organic bromine

from halons and methyl bromide peaked in 1998 and has declined since (WMO, 2007). This observed decrease was solely a result of declines observed for methyl bromide. Bromine (Br) from halons continues to increase, but at slower rates in recent years, see section 3.2.4 on page 30. Additionally, Methyl bromide is a greenhouse gas with a lifetime of 0.7 years and it is 5 times stronger than CO<sub>2</sub>, if the emissions of both gases were equal.

We have calculated the annual trend by use of the model described in Appendix I. The trend and change in the trend is given in Table 2. For the period 2001-2007 there is a reduction in the mixing

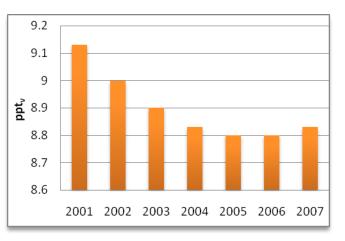


Figure 10: Development of the annual means of Methyl Bromide measured at the Zeppelin Observatory for the period 2001-2007.

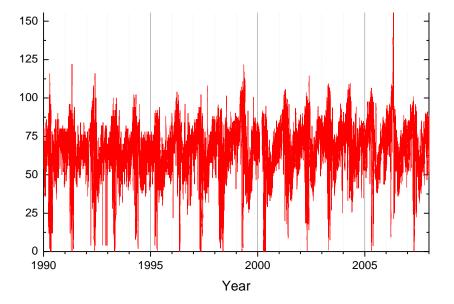
ratio of -0.05 ppt per year, with a very small acceleration in the trend of 0.03 indicating that the trend is expected to be similar, or slightly larger, for the next year (if there are no abrupt changes in sources and sinks). However, the observed changes are small, and this is uncertain.

The development of the annual means for the period 2001-2007 is presented in Figure 10, clearly illustrating the decrease the last years, with a small not significant increase from 2006-2007. In general atmospheric amounts of methyl bromide have declined, beginning in 1999 when industrial production was reduced. By mid-2004, mixing ratios had declined 1.3 ppt (14%) from the peak of 9.2 ppt measured before 1999 (WMO, 2007). Our observations are higher than the global mean values, and the trend is somewhat smaller.

#### 3.1.5 Observations of tropospheric ozone in the period 1990 to summer 2008

Tropospheric ozone (which is the ozone in the lower part of the atmosphere) is a natural constituent of the atmosphere and plays a vital role in many atmospheric processes. It also a greenhouse gas with a radiative forcing of +0.35 W m<sup>-2</sup> (IPCC, 2007) due to changes in the concentrations since 1750. Ozone is not emitted directly to the atmosphere, it is rather produced from precursor gases; the formation of ozone is due to a large number of photochemical reactions taking place in the atmosphere and depends on the temperature, humidity and solar radiation as well as the primary emissions of nitrogen oxides and volatile organic compounds. Anthropogenic emissions of VOC and nitrogen oxides have increased the photochemical formation of ozone in the troposphere. Until the end of the 1960s the problem was basically believed to be one of the big cities and their immediate surroundings. In the 1970s, however, it was found that the problem of photochemical oxidant formation is much more widespread. The ongoing monitoring of ozone at rural sites throughout Europe shows that episodes of high concentrations of ground-level ozone occur over most parts of the continent every summer.

The 1999 Gothenburg Protocol is designed for a joint abatement of acidification, eutrophication and ground-level ozone. The critical levels defined by ECE for protection of vegetation are 150  $\mu$ g/m<sup>3</sup> for hourly mean, 60  $\mu$ g/m<sup>3</sup> for eight-hour mean and 50  $\mu$ g/m<sup>3</sup> for seven-hour mean (9 a.m.–4 p.m.) averaged over the growing season (April-September).



The observed ozone mixing ratios for the period 2001-2007 are shown in the next Figure.

*Figure 11: Observations of ozone in the troposphere for the period 2001 to 31.07.2008 at the Zeppelin observatory. Red dots: daily average concentrations observations.* 

Monthly mean concentrations show a large seasonal variation. In 2006 there was an extreme episode with transport of pollution into the Arctic region and ozone levels as high as ~160  $\mu$ g m<sup>-3</sup>. This was above all critical levels. In 2007 there have been remarkably few episodes, and the maximum ozone level observed was 91  $\mu$ g m<sup>-3</sup> in December 2007.

#### 3.1.6 Observations of CO in the period 2001-2007

Carbon monoxide (CO) is not considered as a direct greenhouse gas, mostly because it does not absorb terrestrial thermal IR energy strongly enough. However, CO is able to modulate the production of methane and tropospheric ozone which are both very important components. The CO sources and emissions have influence on the increasing tropospheric ozone and methane concentrations. CO is closely linked to the cycles of methane and ozone and like methane plays a key role in the control of the OH radical.

The observed CO mixing ratio for the period 2001-2007 are shown in the next Figure.

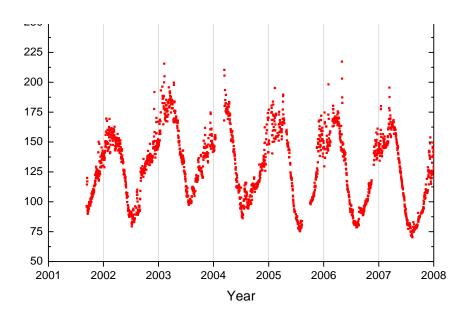


Figure 12: Observations of carbon monoxide (CO) for the period 2001-2007 at the Zeppelin observatory. Red dots: daily averaged observed mixing ratios.

Monthly mean concentrations of CO 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.

The CO concentrations measured at Zeppelin show a decrease during the period, and 2007 was the minimum for the period investigated. This is important to note, as the sources are many and complex, and the level of this compound is important for ozone and methane. Atmospheric CO sources are oxidation of various organic gases (volatile organic compounds, VOC) from sources as fossil fuel, biomass burning, and also oxidation of methane is important. Additionally emissions from plants and ocean are important sources.

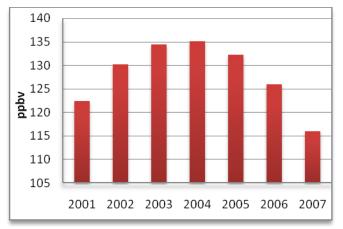


Figure 13: Development of the annual means of CO measured at the Zeppelin Observatory for the period 2001-2007.

The global levels of CO were increasing before mid-1980s, and 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. We calculated a trend of -1.1 ppb per year for the period 2001-2007, and the change in the trend is as high as -3.5 indicating that there is now a considerable acceleration in the decrease of CO for this short time period. The

development of the annual means for the period 2001-2007 is presented in Figure 13, clearly illustrating a maximum in the year of 2004, and a decrease the last years particularly from 2006-2007.

#### 3.2 Greenhouse gases with solely anthropogenic sources

All the gases presented in this chapter have solely anthropogenic sources. These are the manmade greenhouse gases and are called CFCs, HCFCs, HFCs PFCs, SF<sub>6</sub> and halons and the gases did not exist in the atmosphere before the  $20^{th}$  century. Although the gases have much lower concentration levels than most of the natural gases mentioned in the previous section, they are strong infrared absorbers, many of them with extremely long atmospheric lifetimes resulting in high global warming potentials; see Table *1* on page 7.

Some of these gases are ozone depleting, and they are regulated through the Montreal protocol. Additional chlorine from CFCs and HCFCs added to the atmosphere contributes to the thinning of the ozone layer, allowing increased UV radiation to reach the earth's surface, with potential impact not only to human health and the environment, but to agricultural crops as well. In 1987 the Montreal Protocol was signed in order to reduce the production and use of these ozone-depleting substances (ODS) and the amount of ODS in the troposphere reached a maximum around 1995. The amount of most of the ODS in the troposphere is now declining slowly and one expects to be back to pre-1980 levels around year 2050. In the stratosphere the peak is reached somewhat later.

The CFCs, consisting primarily of CFC-11, -12, and -113, accounted for ~62% of total tropospheric Chlorine in 2004 and accounted for a decline of 9 ppt Chlorine from 2003-2004 (or nearly half of the total Chlorine decline in the troposphere over this period) (WMO, 2007).

It is two generations of substitutes for the CFCs, the main group of the ozone depleting substances. The first generation substitutes is now included in the Montreal protocol as they also influence the ozone layer. This is the so-called HCFCs in Table 1 and Table 2. The second-generation substitutes, the HFCs, are included in the Kyoto protocol. The situation now is that the CFCs have started to decline, while their substitutes are increasing, and many of them have a steep increase.

#### **3.2.1** Observations of Chlorofluorocarbons (CFCs) in the period 2001-2007

This section includes the results of the observations of the CFCs: CFC-11, CFC-12, CFC-113, CFC-115. These are the main ozone depleting gases, and the anthropogenic emissions started around 1930s and were restricted in the first Montreal protocol. Figure 14 shows the daily averaged observed mixing ratios of these four CFCs.

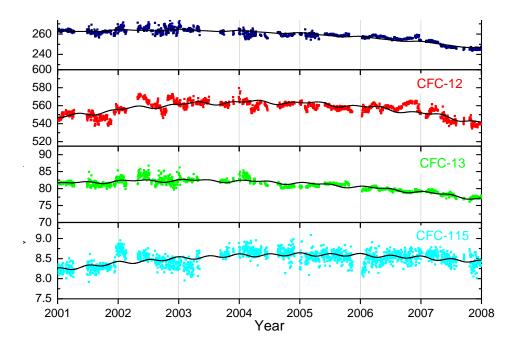


Figure 14: Daily averaged mixing ratios of the monitored CFCs: CFC-11 (dark blue), CFC-12 (red), CFC-13 (green) and CFC-115 (light blue) for the period 2001-2007 at the Zeppelin observatory. The solid lines are modelled background concentrations.

The main sources of these compounds were foam blowing, aerosol propellant, temperature control (refrigerators), solvent, and electronics industry. The highest production of the observed CFCs was around 1985. The life times of the compounds is long as given in Table 1, and also the GWP due to the life time and strong infrared absorption properties is high.

We have used the model described in Appendix I in the calculation of the annual trends, and changes in the trends. The trends per year for the substances CFC-11, CFC12 and CFC-13 are now all negative, given in Table 2. This is the first year CFC-12 has a negative trend for the investigated period (2001-2007) at Zeppelin. For the compound CFC-115 the trend is still positive, +0.04, but the change in trend is negative and thus we expect the trend for 2001-2008 to be negative. In total the development of the CFC levels at the global back-ground site Zeppelin is now very optimistic.

According to WMO (WMO, 2007) the CFC-11 mixing ratios are decreasing at approximately 1.9 ppt/year and CFC-113 are decreasing by approximately 0.8 ppt/yr up to 2005 as a global mean. This is relatively close to our results for the period 2001-2007, but we find a larger reduction for CFC-11, approximately 2.3 ppt/year. In Europe the growth rates for CFC-11 was -2.7 for 2003-2004, in agreement with our results. For CFC-113 the difference is larger, we had only and 0.6 ppt/year now and -0.4 ppt/year for 2001-2006. The difference might be explained by the distribution of the sources, and the very remote location of the Zeppelin observatory.

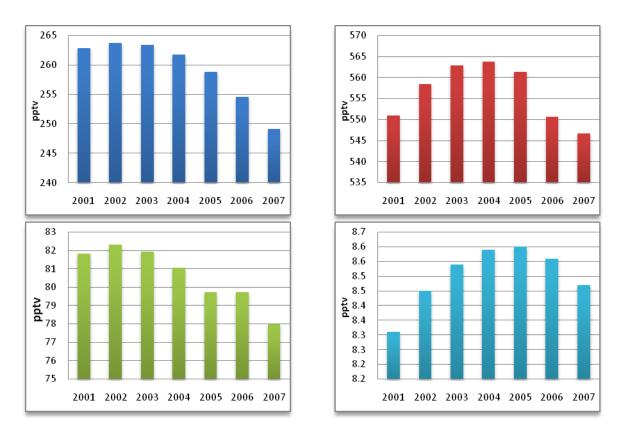


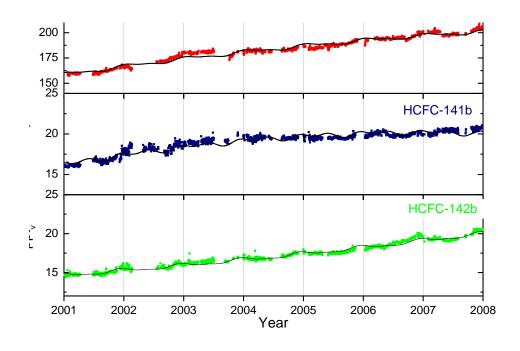
Figure 15: Development of the annual means all the observed CFCs at the Zeppelin Observatory for the period 2001-2007. Upper left panel: CFC-11, upper right panel: CFC-12, lower left panel: CFC-13, lower right panel: CFC-115

The development of the annual means for all the observed CFCs is shown in Figure 15, and this shows a similar tendency for all the compounds; a weak increase in the beginning of the period and a decrease the recent years. CFC-12 is the gas with the highest GWP of the CFCs, 10600, and the second highest of all gases observed at Zeppelin. This means that the warming potential of 1 kg emitted CFC-12 has 10600 times stronger warming effect than 1 kg emitted  $CO_2$  gas. The global averaged atmospheric mixing ratios of CFC-12 have been constant within 1% (5 ppt) since 2000 and some *in situ* column measurements at Northern Hemisphere show that peak values were attained in 2003 (WMO, 2007). This fits well with our observations as illustrated in Figure 15 as CFC-12 (the red diagram) has the maximum in 2003-2004, but the variations since 2001 is a larger than the global average variation.

#### 3.2.2 Observations of Hydrochlorofluorocarbons (HCFCs) in the period 2001-2007

This chapter includes the observations of the following components: HCFC-22, HCFC-141b and HCFC-142b. These are all first generation replacement gases for the CFCs and their lifetimes are rather long. This means that they have potentially strong warming effects, also depending on their concentrations and absorption properties; their GWPs are high (see Table 1). The compound HCFC-142b is the strongest of these gases, and the warming potential is 2400 times stronger than  $CO_2$ , per kg gas. These gases do also contain chlorine, and thus are contributing to the depletion of the ozone layer. The HCFCs accounted for 6% of the total tropospheric chlorine in 2004 versus 5% of the total in 2000 (WMO, 2007).

The daily averaged observations of these gases are shown in Figure 16 for the period 2001-2007.

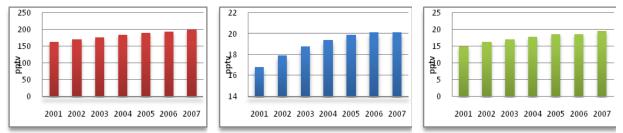


*Figure 16: Daily average mixing ratios of the monitored HCFCs: HCFC-22 (red), HCFC-141b (dark blue) HCFC-142b (green) for the period 2001-2007 at the Zeppelin observatory. The solid lines are modelled background concentrations.* 

The trends per year for the compounds HCFC-22, CFC-141b and HCFC-142b are all positive, particularly for HCFC-22 as given in Table 2. HCFC-22 is the most abundant of the HCFCs and is currently increasing at a rate of 6.1 ppt/year. In comparison, the global mean increase for 2000-2004 was +4.9 ppt/year according to WMO, (WMO, 2007). HCFC-141b and HCFC-142b mixing ratios increased by 0.6 ppt/yr and 0.8 ppt/year, respectively.

It is worth mentioning that the changes in trends are negative for HCFC-22 and HCFC-141b, meaning that the increase in the concentrations is slowing down. This is not the case for HCFC-142b, which still has a slight acceleration in the trend. The rates of increase for all three of these HCFC substances are significantly slower than projected in the previous Ozone Assessment (WMO, 2007).

The next Figure shows the annual means for the full period for all these compounds, clearly illustrating the development; and increase which now shows signs of slowing down.

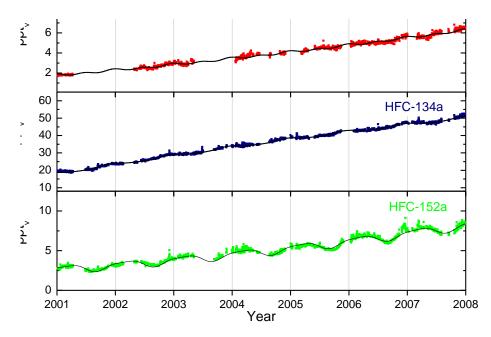


*Figure 17: Development of the annual means the observed HCFCs at the Zeppelin Observatory for the period 2001-2007. Red: HCFC-22, Blue:H CFC-141b, and green: HCFC-142b.* 

The main sources of these gases are temperature control (refrigerants), foam blowing and solvents, as for the CFCs, which they suppose to replace. All these gases are regulated through the Montreal protocol as they all contain Chlorine. The emissions of the gases are now frozen, but not completely phased out. With lifetimes in the order of 10-20 years it is central to monitor the levels in the future as they have an influence both on the ozone layer, and are strong climate gases.

#### 3.2.3 Observations of Hydrofluorocarbons (HFCs) in the period 2001-2007

The substances called HFCs are the so called second generation replacements of CFCs, which means that they are considered as better alternatives than HCFCs described in the previous section with respect to the ozone layer. This category includes the following components: HFC-125, HFC-134a, HFC-152a with lifetimes in the order of 1.4-30 years. These substances do not contain Chorine thus they do not have a direct influence on the ozone layer. HFC-152a has short life time and is mainly destroyed in the lowest part of the atmosphere by photolysis and reactions with OH. The seasonal cycle in the observed mixing ratio of these substances is caused by the variation in the incoming solar radiation and is clearly visible in the time series shown in Figure 18 for HFC-152a.



*Figure 18: Daily average concentrations of the monitored CFCs: HFC-125 (red), HFC-134a (dark blue), HFC-152a (green) for the period 2001-2007 at the Zeppelin observatory. The solid lines are modelled background concentrations.* 

Even if these compounds are better alternatives for the protection of the ozone layer as they do not contain Chlorine or Bromine, they are still highly potent greenhouse gases. 1 kg of the gas HFC-125 is as much as 3400 times more powerful greenhouse gas than  $CO_2$ . But still their concentrations are rather low, but strongly increasing as our results show. This is also clearly illustrated in the Figure showing the development of the annual means. The gases are continuously increasing with the same change per year as earlier.

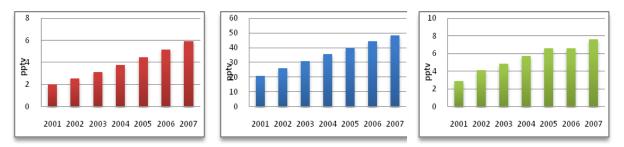
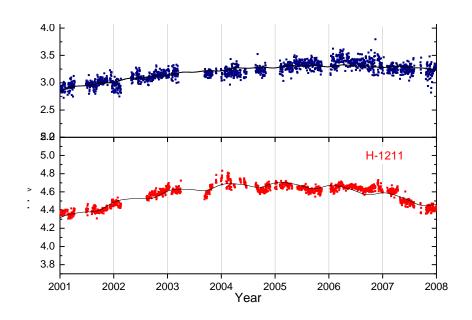


Figure 19: Development of the annual means the observed HFCs at the Zeppelin Observatory for the period 2001-2007. Red: HFC-125, Blue: HFC-134a, and green: HFC-152a.

The three main HFCs are HFC-23 (not measured at Zeppelin), HFC-134a and HFC152a, with HFC-134a being the most widely used refrigerant (temperature control) and in air conditioners in cars. Since 1990, when it was almost undetectable, concentrations of HFC-134a have risen massively. For the period 2001-2007 we find an annual increase per year of 4.6 ppt, which leaves this compound as the one with the second highest change per year for the all the gases observed at Zeppelin. The mixing ratios of HFC-125, HFC-134a, HFC-152a have increased by as much as 190%, 133% and 169% respectively since 2001. Due to the large increase it is relevant to calculate the radiative forcing of these observed changes. Based on the assumption that these changes are the same at all locations (constant geographical distribution) we find that the total radiative forcing for the change in the period 2001-2007 is 0.006 W m<sup>-2</sup> for the three gases. Thus the contribution from the recent man made changes in these gases is considered as small. This is explained by the (still) low mixing ratios of the compounds.

#### 3.2.4 Observations of Halons in the period 2001-2007

Halons include the following components: H-1301, H-1211. These substances contain Bromine, also contribution to the depletion of the ozone layer. The compounds are regulated trough the Montreal protocol, and are now phased out. The main source of these substances was fire extinguishers. Figure 20 presents the daily average concentrations of the monitored halons.



*Figure 20: Daily average concentrations of the monitored halons: H-1301 (blue in the upper panel) and H-1211 (Red in the lower panel) for the period 2001-2007 at the Zeppelin observatory. The solid lines are modelled background concentrations.* 

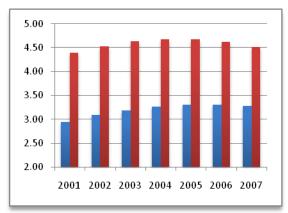


Figure 21: Development of the annual means the observed Halons at the Zeppelin Observatory for the period 2001-2007. Red: Halon-1211, Blue: H-1301.

By use of the model described in Appendix I we have calculated the annual trends, and changes in trends, given in Table 2. The trends for the period 2001-2007 is increasing for both substances, with a very small reduction in the rates indicating that the trend is expected to be smaller the next years (if there are no abrupt changes in sources and sinks).

The development of the annual means are shown in the Figure to the left, and as can be seen the mixing ratios are quite stable over the period explained by low emissions and relatively long lifetimes (11 years for H-1211 and 65 years for H-1301.). According to the last Ozone Assessment (WMO, 2007) it is

currently unclear whether atmospheric mixing ratios of halon-1301 continue to increase. The global average atmospheric increase in halon-1211 was 0.06 ppt/year in 2000-2004 were about half those in 1996-2000. This agrees well with our observations in the Arctic region.

#### 3.2.5 Observations of other chlorinated hydrocarbons in the period 2001-2007

This section includes observations of the components: Trichloromethane (also called Methyl chloroform) ( $CH_3CCl_3$ ), Dichloromethane ( $CH_2Cl_2$ ), Chloroform ( $CHCl_3$ ), Trichloroethylen ( $CHClCCl_2$ ), Perchloroethylene ( $CCl_2CCl_2$ ). The main source of all these substances is solvents. The daily averaged concentrations are shown in Figure 22.

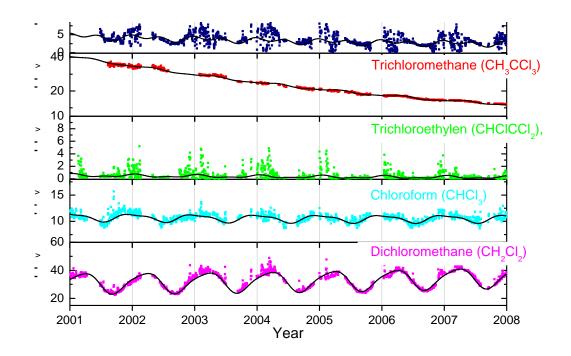
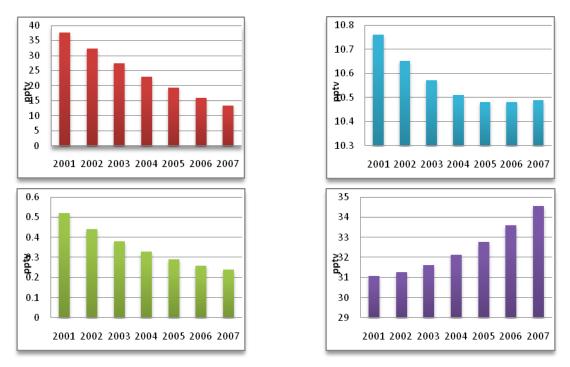


Figure 22: Daily average concentrations chlorinated hydrocarbons: From the upper panel: Perchloroethylene (dark blue) Trichloromethane (red), Trichloroethylen (green), Chloroform (light blue) and Dichloromethane (pink) for the period 2001-2007 at the Zeppelin observatory. The solid lines are the modelled background concentrations.

The large seasonal variations shown in the daily averaged concentrations of the compounds reflect the short lifetimes. The compounds do have relatively low GWP, with Methyl chloroform as the highest (30). Figure 23 shows the annual means for the period 2001-2007. For the substances Perchloroethylene, Trichloromethane and Trichloroethylen the development are similar with homogenous decrease. This is also reflected in the calculated trends, all are negative and Trichloromethane has the highest reductions with a change of 4.1 ppt per year for the period 2001-2007. For Dichloromethane there is an increase of 11% since 2001.

Trichloromethane (CH<sub>3</sub>CCl<sub>3</sub>) has continued to decrease and contributed 13.5 ppt, or more than half, of the overall decline observed for total tropospheric Cl in 2003-2004. It is currently still the largest contributor to the decline in tropospheric chlorine. Globally averaged surface mixing ratios were 22.6 ppt in 2004 versus 46.4 ppt in 2000 (WMO, 2007). This is close to our observations.



*Figure 23: Development of the annual means all the Chlorinated hydrocarbons. From the upper panel: Trichloromethane (red), Perchloroethylene (blue), Trichloroethylen (green), and Dichloromethane (violet) for the period 2001-2007.* 

#### 3.2.6 Perfluorinated compounds

The only perfluorinated compound measured at Zeppelin is Sulphurhexacloride, SF<sub>6</sub>. This is an extremely potent greenhouse gas emitted to the atmosphere mainly from the production of magnesium and electronics industry. The atmospheric lifetime of this compound is as much as 3200 years, and the global warming potential is 22200, which means that the emission of 1 kg of this gas has a warming potential which is 22200 times stronger than 1 kg emitted CO<sub>2</sub>. The other perfluorinated compounds are also very powerful greenhouse gases thus we plan to extend the monitoring programme with Carbon Tetrafluoride (CF<sub>4</sub>) and possibly also Hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) from 2009, when we have new and improved instrumentation installed at Zeppelin. The current instrumentation is not well suited for measurements of SF<sub>6</sub> thus there are larger uncertainties in this compound than in most of the other compounds reported. The daily averaged concentration of SF<sub>6</sub> is presented in Figure 24. Note that the variations through the year is not due to seasonal variations, rather it is instrumental adjustments.

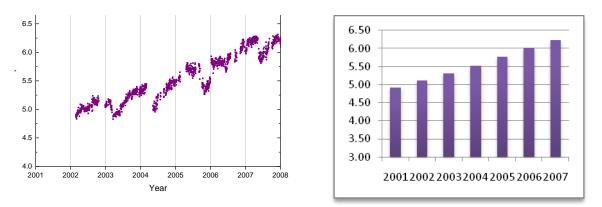
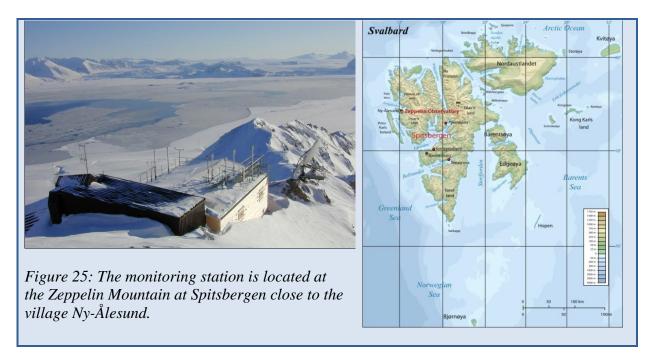


Figure 24: Daily average concentrations of  $SF_6$  for the period 2001-2007 to the left, and the development of the annual mean concentrations in the right panel.

### **3.3** The Zeppelin observatory

The monitoring observatory is located in the Arctic 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 a.s.l 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.



The unique location of the station makes it an ideal platform for the monitoring of global atmospheric change and long-range transport of pollution. 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. This includes greenhouse gases, ozone, persistent organic pollutants, aerosols and others.
- Characterization of the arctic atmosphere and studies of atmospheric processes and changes

The measurement activities at the Zeppelin station contribute 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 atmospheric change (NDAC under UNEP and WMO)
- Global Atmospheric Watch (GAW under WMO)
- Arctic Monitoring and Assessment Programme (AMAP)

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 removed to give place to a new modern station that was opened in May 2000. The building contains several separate laboratories, some for permanent use by NILU and Stockholm University, 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.

### 3.3.1 NILU's activities at the Zeppelin observatory

NILU performs measurements of more than 20 greenhouse gases including halogenated greenhouse gases, methane and carbon monoxide. In Appendix I are details about sampling techniques and frequency of observations described. 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 Precision-Filter-Radiometer (PFR) sun photometer. This instrument gives the aerosol optical depth (AOD). AOD is a measure of the aerosols attenuation of solar radiation in the total atmospheric column.

The station at Zeppelin Mountain is also used for a wide range of other 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 ozone. Zeppelin observatory is also widely used in campaigns as during the International Polar Year.

### **3.3.2** Measurements of CO<sub>2</sub> at Zeppelin observatory

At the Zeppelin station carbon dioxide (CO<sub>2</sub>) is measured by Stockholm University (SU) (Institute of Applied Environmental Research, ITM).

SU maintain an infrared  $CO_2$  instrument measuring  $CO_2$  continuously. The instrument has been in operations 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 in addition to  $CO_2$ .

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 timescales 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>.

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 instrument 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.

## 4 Observations of total aerosol load at Ny-Ålesund, Svalbard

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 regions and respond quickly to changes in emissions as their lifetime is short, in the order of days-weeks.

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.

### 4.1 AOD measurements in 2007 at Ny-Ålesund

Hourly AOD values measured in Ny-Ålesund with the PFR-instrument are presented in Figure 12 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 in July and September. These are caused by long-range transport of aerosols into the Arctic.

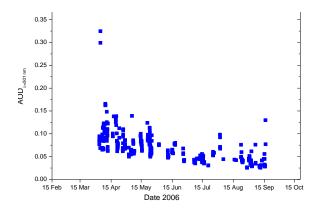


Figure 26: Hourly AOD values measured in Ny-Ålesund during 2007.

Table 3 gives an overview of the annual and seasonal mean for AOD at 501 nm and the Ångstrøm exponent. Maximum value for the AOD and the number of hours with observations is also included. Despite the low numbers of observations, the elevated levels in spring are visible in Figure 12 and in the Table below in the mean AOD and max AOD for the spring months.

Table 3: Annual and seasonal mean values of AOD at 501 nm together with the Ångstrøm exponent in Ny-Ålesund in 2007. The numbers in parenthesis indicates the uncertainty (1  $\sigma$ ).

	Mean AOD <sub><math>\lambda=501 \text{ nm}</math></sub> (1 $\sigma$ )	Max AOD <sub>λ=501 nm</sub>	Ångstrom exponent	Number of hours with observations
Annual	0.069 (0.03)	0.325	1.547	330
March-May	0.087 (0.03)	0.325	1.508	187
June-Aug	0.050 (0.01)	0.098	1.634	97
Sept-Oct	0.038 (0.02)	0.13	1.519	46

The Ångstrøm 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 are small compared to primary local source aerosols as sea salt. These are called secondary aerosols. 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 and thus have higher Ångstrøm exponent. In 2007

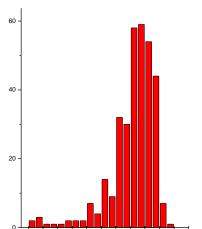


Figure 27: The relative frequency of hourly averaged Ångstrøm exponents,  $\alpha$ , during 2007.

the smallest aerosols are found during summer indicating that there might be aerosol production in the region or transport from source region and less maritime aerosol produced e.g. by sea spray.

In Figure 27 hourly relative frequencies of the Ångstrøm exponents,  $\alpha$ , during 2007 are displayed. The  $\alpha$  values show a distinct peak centered at  $\alpha = 1.60$ . More than 90% of the  $\alpha$  is in the range from 1.05-2, and around 10% of the Ångstrøm exponents are below 1.0 in Ny-Ålesund, the typical value for larger marine aerosols. This is much less than in 2006 where 30% of the values were in this range. The high  $\alpha$  values imply large loading of fine aerosols typical for long-range transport.

### 4.2 AOD measurements 2002-2007

Figure 28 presents the AOD measurements at 501 nm in Ny-Ålesund for the years 2002-2007. The AOD values are, as expected, considerable higher during the Arctic haze period for all

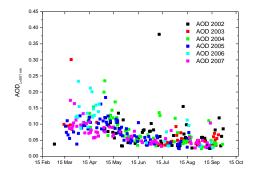


Figure 28: Daily average aerosol optical depth (AOD) measured in Ny-Ålesund during 2002-2007.

years. Yet, Figure 14 illustrates that there are several episodes during the years with short-term elevated AOD values in the summer and autumn as 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, were transported into the region and very likely explain the elevated AOD levels. Furthermore Stohl et al. (2007) showed that agricultural fires in Eastern Europe resulted in elevated pollution levels in Arctic in spring 2006 and Lund Myhre et al. (2007) found that these aerosol had a strong

cooling effect on the Arctic during this period, with a moderate warming effect when the aerosol layer were above snow covered surface areas.

The time series of five years is 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 4. The results show clear seasonal variations and minor variations from year to year.

Table 4: Annual and seasonal mean values for the period March–May and June–August for all years with observations. 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)
2006	$0.14 (17) \sigma = 0.004$	$0.04 (10) \sigma = 0.020$	0.10 (30) $\sigma = 0.006$	0.23 (1 April)
2007	0.12 (28) $\sigma = 0.034$	0.06 (25) $\sigma = 0.017$	0.12 (61) $\sigma = 0.034$	0.22 (9 April)

## 5 Regional emissions and the influence on the observations

Analyses of the air mass origin are important for the understanding of the observed levels of the gases. We have analysed the origin of the air arriving at Zeppelin in 2007. 7 days backward trajectories from the European Center for Medium-Range Weather Forecasts (ECMWF) have been used to investigate the major transport pathways into the region.<sup>3</sup> The origin of the air arriving at Zeppelin is categorised in following 6 sectors:

- Arctic region: Clean Arctic air: Air mass trajectories with all trajectory points north of 65°N were classified as Arctic
- Atlantic sector: Clean marine air: Air mass trajectories with all trajectory points between 10°W and 70°W and from south of 60°N.
- North American sector: Polluted air: If at least 50% of the trajectory points are between 70°W and 180°W, and from south of 60°N.
- **European sector:** Polluted air: If at least 50% of the trajectory points were between 10°W and 30°E, and from south of 60°N.
- **Russian sector:** Polluted air: If air mass trajectories with all points between 30°E and 180°E and from south of 60°N the sector were classified as 'Russian' sector.
- **Undefined sector:** 20% the trajectories do not come from a distinct sector. This is classified as 'undefined'.

The Arctic and Atlantic sector are assumed to have minimal influence of pollution. There are no industrial sources in these areas, and one can say that the air is 'clean'. Background values are defined from those 'clean air' areas with 6 out of 8 trajectories (sampling day  $\pm 12$  hours) within the sector, as described above.

The Table below shows the portion of the polluted and clean air arriving at Zeppelin observatory for the years 2001-2007.

Table 5: The distribution of polluted and clean air arriving at Zep	ppelin in the period 2001-
2007.	

	2001	2002	2003	2004	2005	2006	2007
Total days	365	365	365	366	365	365	365
Clean air	206	203	213	174	186	195	246
% days with clean air	56.4	55.6	58.4	47.5	51.0	53.4	67.4

<sup>&</sup>lt;sup>3</sup> The spatial resolution is T106, which correspond to a latitude/longitude resolution of 1.125x1.125 degrees, the temporal resolution is 6 hours, and 60 levels (91 levels after February 2006) are available in the vertical direction. The data sets used are so-called analysis, which is a combination of observations and numerical calculations. This includes measurements from satellites, radio sondes, buoys, weather stations, etc. which are assimilated into a meteorological model that produce an estimate of the state of the atmosphere at a given time.

In 2007 there were relatively few episodes with polluted air transported to Zeppelin and no extreme episode as the record one observed in 2006 (Stohl et al, 2007, Lund Myhre et al 2007). Rather it is important to emphasise the high frequency of days with air categorised as clean arctic marine air (67%) for 2007. This is air from the Atlantic region and north of 65 degrees from northern part of Scandinavia, Russia, Greenland, USA and Alaska. This means that the observations at Zeppelin were less influenced by long range transport in 2007 than previous years.

### 5.1 Regional emissions and the elevated methane levels

We have performed a more detailed analysis of the air masses for the days and periods with elevated methane levels in 2007. In Figure 29 are the methane observations for the period 2001-2007 shown together with an indication if the air masses are considered as clean Arctic and Atlantic air or polluted air.

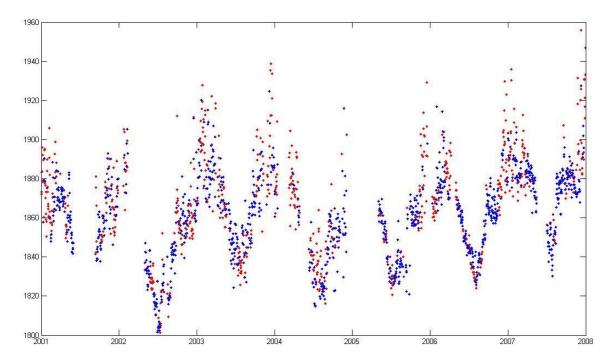
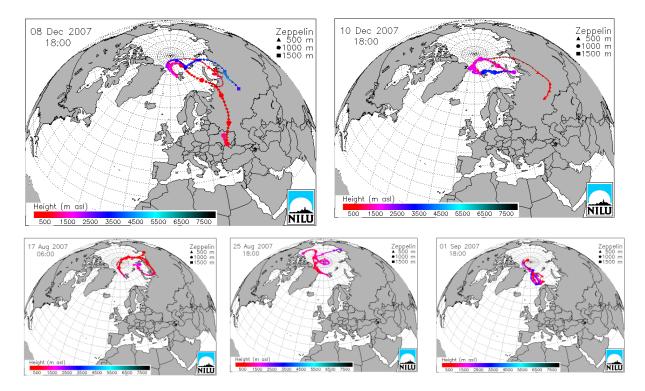


Figure 29: Observations of methane for the period 2001-2007 at the Zeppelin observatory. Blue dots: air mass origin is from a clean sector, red dots: the air mass origin is from a polluted sector.

The blue dots represent the background methane levels which mean that the air masses have originated from the Arctic or Atlantic region. The red dots represent the methane observations when the air masses arriving at Zeppelin originate from a polluted region: North America, Europe or Russia. As can be seen in 2007 a large portion of the air masses arriving at Zeppelin originate for the Arctic and Atlantic sector, particularly during the summer and the autumn. Further, the peak episodes are due to pollution transported from lower latitudes.

The next Figure shows 5 different plots for selected days. In the upper panel are trajectories for the days with maximum methane mixing ratio showed, and the lower panel are typical trajectories for the elevated period in August and September.



*Figure 30: Trajectory plots for selected periods with elevated methane levels at Zeppelin in 2007.* 

The maximum methane mixing ratio ever detected at Zeppelin was on 10<sup>th</sup> December 2007 and was as high as 1956 ppb. At this day, and the days before, air from North and central Russia, and east Europe (8<sup>th</sup> December) arrived at Zeppelin. This is a typical situation for long range transport of pollution from the continents industrialised regions.

The lower panel shows the typical situation for the period in August with elevated levels. The air was quite stable north of 65 degrees and circulates the Arctic region following a path relatively close to the surface. The air masses were in contacted with the surface particularly in the northern part of Russia and Greenland during this period. The analysis of the source regions and influence on the methane levels at Zeppelin will continue, and no conclusions can be drawn at this point.

## 6 Greenhouse Gas Monitoring Networks

## 6.1 SOGE

SOGE is an integrated system for observation of halogenated greenhouse gases in Europe and was funded in 2001-2003. 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 airparcels 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.

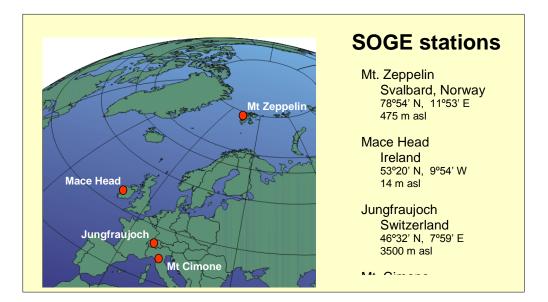


Figure 31: The SOGE climate gas monitoring stations.

## 6.2 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<sub>2</sub> gases in the Kyoto Protocol to mitigate climate change.

The scientific objectives of AGAGE are considerable importance in furthering our understanding 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<sub>2</sub>O, CH<sub>4</sub>, CO, H<sub>2</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CHBr<sub>3</sub>, CH<sub>3</sub>I, CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>2</sub>CCl<sub>2</sub> and CHCl<sub>3</sub> 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<sub>3</sub>CCl<sub>3</sub> and other hydrohalocarbons from continuous measurements of their concentrations together with industrial estimates of their emissions.
- To optimally determine, using CH<sub>4</sub> and N<sub>2</sub>O 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<sub>4</sub> and N<sub>2</sub>O.
- 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 32: The AGAGE network of monitoring stations.

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# Appendix I

## Description of instruments, methods and trend analysis

Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway - Annual report 2007 (TA-2480/2009)

### Description of instruments and methods

In this appendix are the instrumental methods used for the measurements of the various greenhouse gases presented. Additionally we explained the theoretical methods used in the calculation of the trends and how the annual mean values presented in Table 2 are calculated in the end of the section.

#### Instrumental description

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.

Component		Instrument and method	Time res.	Calibration procedures	Comment
Methane	CH₄	GC-FID	1 h	Hourly, working std. calibrated vs. GAW std.	Data coverage 2007: 86% Instrument down for a longer period May-June due to instrument breakdown, requiring major repairs and wait for new spare parts.
Carbon monoxide	со	GC-MgO/UV	1 h	Every 2 hours, working std. calibrated vs. GAW std.	Data coverage 2007: 95%
Carbondioxide	CO <sub>2</sub>		1 h		CO2 measurements performed by ITM Stockholm University (SU)
CFC-11 CFC-12 CFC-113 CFC-115 HFC-125 HFC-134a HFC-152a HCFC-22 HCFC-141b HCFC-142b H-1301 H-1211 Methyl Chloride Methyl Bromide Methyl Bromide Methylendichloride Chloroform Methylchloroform TriChloroethylene Perchloroethylene Sulphurhexafluoride		ADS-GC-MS	4 h	Every 2 hours, working std. calibrated vs. AGAGE std.	Data coverage 2007: 67% Instrument down for longer periods in January due to Gas Chromatograph breakdown, and in August-September due to Mass Spectrometer breakdown, requiring major repairs and wait for new spare parts.
Ozone	O <sub>3</sub>		5 min		

The amount of particles in the air is monitored by a continuous aethalometer (SU) and by the use of a Precision-Filter-Radiometer (PFR) sun photometer (NILU). The aethalometer measures the total amount of particles at ground level, while the sun photometer measures the amount in 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<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, (NO<sub>3</sub><sup>-</sup> + HNO<sub>3</sub>) and (NH<sub>4</sub><sup>+</sup> + NH<sub>3</sub>), main compounds in precipitation, mercury, persistent organic pollutants (HCB, HCH, PCB, DDT, PAH etc.), as well as tropospheric and stratospheric ozone.

# Observations of Aerosol Optical Depth: Experimental details regarding the Precision Filter Radiometer (PFR) in 2007

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, 474 m asl). The PFR has been in operation since May 2002. In Ny-Ålesund the polar night lasts from 26<sup>th</sup> October to 16<sup>th</sup> 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 centered 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 in the calculations. The low number of days with measurements is caused by bad weather conditions. The number of days where measurements can be performed is reduced due to cloudy or foggy weather conditions as the measurements are dependent on direct solar radiation.

### CO<sub>2</sub> measurements performed by ITM Stockholm University (SU)

At the Zeppelin station carbon dioxide (CO<sub>2</sub>) 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<sub>4</sub>, CO, H<sub>2</sub>, N<sub>2</sub>O and SF<sub>6</sub> data for the Zeppelin station.

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 timescales 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>.

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.

### Model studies: Calculation of trends

### **Calculation of trends**

To calculate the annual trends the observations have been fitted as described in Simmons et al. (2006) by an empirical equation of Legendre polynomials and harmonic functions with linear, quadratic, and annual and semi-annual harmonic terms:

$$f \mathbf{q} = a + b \left(\frac{N}{12}\right) \cdot P_1 \left(\frac{t}{N} - 1\right) + \frac{1}{3} \cdot d \left(\frac{N}{12}\right)^2 \cdot P_2 \left(\frac{t}{N} - 1\right) + c_1 \cdot \cos \mathbf{q} \cdot \pi \mathbf{q} + s_1 \sin \mathbf{q} \cdot \pi \mathbf{q} + c_2 \cos \mathbf{q} \cdot \pi \mathbf{q} + s_2 \sin \mathbf{q} \cdot \pi \mathbf{q}$$

The observed f can be expressed as functions of time measures from the 2N-months interval of interest. The coefficient a defines the average mole fraction, b defines the trend in the mole fraction and d defines the acceleration in the trend. The c and s define the annual and interannual cycles in mole fraction. N is the mid-point of the period of investigation. P<sub>i</sub> are the Legendre polynomials of order i.

### Determination of background data

Based on the daily mean concentrations an algorithm is selected to find the values assumed as clean background air. If at least 75% of the trajectories within +/- 12 hours of the sampling day are arriving from a so-called clean sector, defined below, one can assume the air for that specific day to be non-polluted. The remaining 25% of the trajectories from European, Russian or North-American sector are removed before calculating the background.

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# Appendix II

## The Montreal and Kyoto Protocol

Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway - Annual report 2007 (TA-2480/2009)

### Background on the Montreal protocol for the protection of the ozone layer

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 byproducts of societal activities, such as energy conversion and agriculture, rather than production and consumption.

#### 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 Coordinating Committee on the Ozone Layer (CCOL 1977) were reviewing results of atmospheric measurements and the models using them, and developing projects to extend understanding of ozone layer behavior.

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. Today about 190 countries have ratified the protocol.

The Protocol, which came into force on 1<sup>st</sup> 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.

### Amendments and Adjustments to the Protocol

### 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<sub>2</sub>), 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.

### 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.

### 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<sub>4</sub> and CCl<sub>3</sub>CH<sub>3</sub> 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.

### 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<sub>4</sub> and CCl<sub>3</sub>CH<sub>3</sub>,: 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.

### 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 phase-out of a new species Bromochloromethane (CH<sub>2</sub>BrCl) in 2002

### 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<sup>-1</sup> 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<sup>nd</sup> 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.

### 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<sub>2</sub>), which accounts for 55% of the increase in radiative forcing since pre-industrial times. Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), together, are calculated to contribute 21% and halocarbons the remaining 11%. 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<sub>2</sub> 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<sub>2</sub>. The problem that the effect of CO<sub>2</sub> 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<sub>2</sub> 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<sub>6</sub>).

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<sub>6</sub>.

### 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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Greenhouse monitoring at the Zeppelin station Annual report 2007

#### Sammendrag – summary

Rapporten presenterer aktiviteter og måleresultater fra klimagassovervåkingen ved Zeppelinobservatoriet på Svalbard for årene 2001-2007.

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The report summaries the activities and results of the greenhouse gas monitoring at the Zeppelin observatory situated on Svalbard in Arctic Norway during the period 2001-2007.

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4 emneord	4 subject words
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Statlig program for forurensningsovervåking omfatter overvåking av forurensningsforholdene i luft og nedbør, skog, vassdrag, fjorder og havområder. Overvåkingsprogrammet dekker langsiktige undersøkelser av:

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

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

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