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Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway

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Greenhouse gas monitoring at the Zeppelin station, Svalbard, Norway

Rapport
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Annual report 2008

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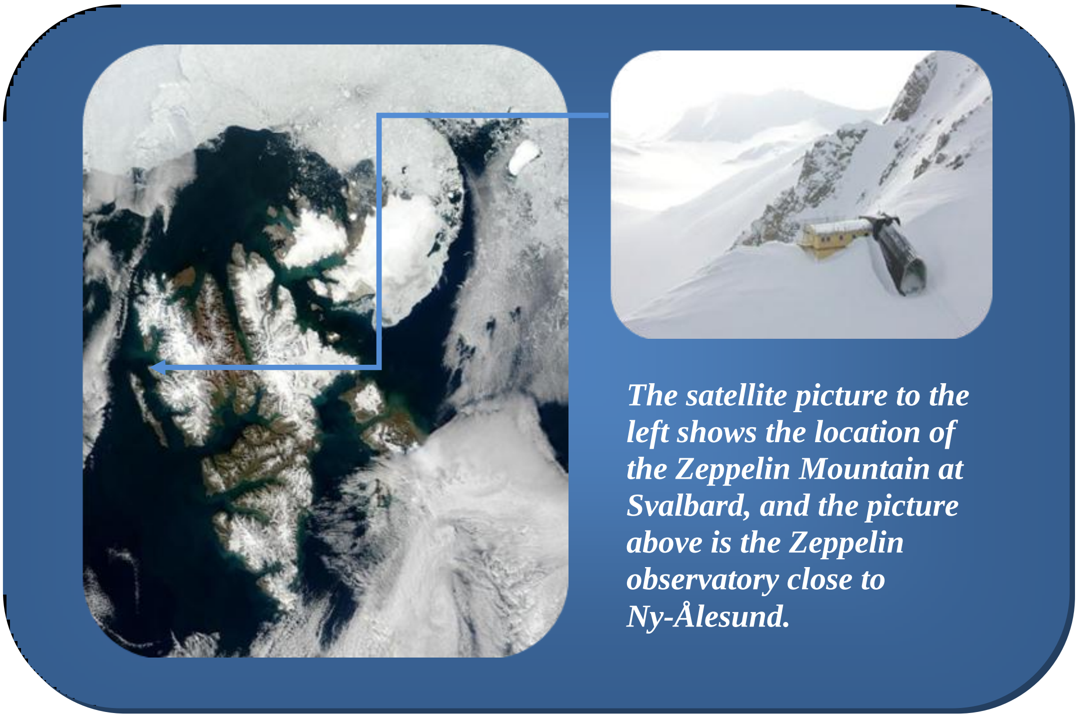
Preface

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.



The satellite picture to the left shows the location of the Zeppelin Mountain at Svalbard, and the picture above is the Zeppelin observatory close to Ny-Ålesund.

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_6).

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_4), hydrofluorocarbons (HFC), sulphurhexafluoride (SF_6). Additionally carbon monoxide (CO) and tropospheric ozone (O_3) 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_2) 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 2008, and comprises a trend analysis for the period 2001-2008.

Kjeller, December 2010

Cathrine Lund Myhre
Senior scientist and project manager

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1. Summary

This annual report describes the activities and main results of the programme "*Greenhouse gas monitoring at the Zeppelin station at Svalbard in the Norwegian Arctic*" for 2008. This 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 gases also have strong ozone depleting effect.

Table 1 summarises the main results and lists all measured gases, their annual mean values the first and the last year, and the trends for the period 2001–2008.

Table 1: Key findings; *Greenhouse gases measured at Ny-Ålesund; their trends, lifetimes, global warming potential (GWP) and relevance to the Montreal and Kyoto Protocols. All concentrations[1] are in pptv, except for methane and carbon monoxide (ppbv) and carbon dioxide (ppmv).*

Compound	**Formula**	**Life-time (years)**	**GWP[2]**	**2001**	**2008**	**Trend / Year**	Montreal or Kyoto Protocol	**Comments on use for the halocarbons**
Methane	CH_4	12.0[3]	25	1858	1884	**+4.1**	**K**	
Carbon monoxide	CO	Months		125.9[4]	122.9	**-1.70**		
Carbondioxide[5]	CO_2		1	370.9	384.1[5]	**+2.3**	**K**	
Chlorofluorocarbons								
CFC-11	CCl_3F	45	4750	263	244	**-2.8**	**M** phased out	foam blowing, aerosol propellant
CFC-12	CCl_2F_2	100	10900	549	537	**-2.1**	**M** phased out	temperature control
CFC-113	CCl_2FCClF_2	640	6130	82	77	**-0.8**	**M** phased out	solvent, electronics industry
CFC-115	$C_2 F_5Cl$	1700	7370	8.3	8.4	**+0.01**	**M** phased out	temperature control, aerosol propellant
Hydrochlorofluorocarbons								
HCFC-22	$CHClF_2$	12	1810	161	208	**+6.2**	**M** freeze	temperature control, foam blowing
HCFC-141b	$C_2H_3FCl_2$	9.3	725	16.6	21.1	**+0.55**	**M** freeze	foam blowing, solvent
HCFC-142b	CH_3CF_2Cl	17.9	2310	14.9	21.1	**+0.84**	**M** freeze	foam blowing
Hydrofluorocarbons								
HFC-125	C_2HF_5	29	3500	2.0	6.9	**+0.69**	**K**	temperature control
HFC-134a	CH_2FCF_3	14	1430	20.7	53.8	**+4.62**	**K**	temperature control, foam blowing, solvent, aerosol propellent
HFC-152a	$C_2H_4F_2$	1.4	124	2.9	8.7	**+0.83**	**K**	foam blowing
Halons								
H-1211	$CBrClF_2$	16	1890	4.4	4.4	**+0.00**	**M** phased out	fire extinguishing
H-1301	$CBrF_3$	65	7140	3.0	3.3	**+0.04**	**M** phased out	fire extinguishing
Halogenated compounds								
Methylchloride	CH_3Cl	1.0	13	507	523	**+0.86**		natural emissions (algae)
Methylbromide	CH_3Br	0.7	5	9.3	8.15	**-0.10**	**M** freeze	agriculture, natural emissions (algae)
Dichloromethane	CH_2Cl_2	0.38	8.7	31.0	37.8	**+0.84**		solvent
Chloroform	$CHCl_3$	0.5	30	10.8	10.4	**-0.04**		solvent
Methylchloroform	CH_3CCl3	5	146	37.6	11.0	**-3.83**	**M** phased out	solvent
Trichloromethane	C_2HCl_3			0.6	0.4	**-0.04**		solvent
Perchloroethylene	C_2Cl_4			4.4	2.74	**-0.24**		solvent
Sulphurhexafluoride	SF_6	3200	22800	5.0	6.6	**+0.24**	**K**	Mg-production, electronics industry

[1] The term ^{m}ixing 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.
[2] GWP (Global warming potential) 100 years time period, $CO_2 = 1$
[3] The lifetimes for CH_4 are adjustment times including feedbacks of indirect effects on the lifetime.
[4] CO measurements started late in 2001, thus the first year is the value for 2002.
[5] Measurements of CO_2 is performed by Stockholm University. Their results were not available in time for the report, thus the value 384.1 ppm is for 2007.

The lifetimes and GWPs in Table 1 are updated in accordance with the 4th Assessment Report of the IPCC. Trends are calculated for the period 2001–2008 and are given in mixing ratio per year. Further details and interpretations are presented in section 3 of the report.

Greenhouse gases regulated through the Kyoto protocol – Key findings from the Zeppelin observatory

The report includes the 6 greenhouse gases or groups of gases regulated through the Kyoto protocol. The key findings are:

- ***Methane – CH_4:*** In 2008 the **mixing ratios of methane reached new record levels** with an annual mean value of 1884 ppb. This is an increase of 0.34% since 2007, a continuation of the increase during the last years at Zeppelin. Also the global mean methane level reached a new record level in 2008, in average there was a global increase of 0.39% from 2007 (WMO, 2009).

The increase at the Zeppelin observatory since 2004 is around 1.4%. We consider this as a relatively large change compared to the development of the methane levels in the period from 1998-2005; the change was close to zero for this period both at our observatory and globally, according to IPCC (Forster et al, 2007).

Currently there is no clear explanation for the increase in methane after 2004. A probable explanation could be increased methane fluxes from wetlands, both in the tropics as well as in the Arctic region. Melting permafrost but also methane clathrates (also called methane hydrates) in the Arctic Ocean might be new and significant methane emission sources initiated by the observed temperature increase the last years. If this should be the case, it would be an alarming development.

An immediate extension of the monitoring of methane, focusing in particular on identification of possible sources, is needed to improve our current understanding of the ongoing processes. Isotopic measurements of methane at Zeppelin combined with transport modeling will be a highly powerful tool to distinguish between methane from various sources as gas fields, wetland and clathrates.

Methane is measured from space by satellites. Analysis done with the measurements of CH_4 from the Zeppelin observatory shows that the current satellite data are not capable of providing the temporal and spatial resolution needed in order to quantify and understand near-surface variations in $CH_{4.}$ Since there is great uncertainty and also potentially large emissions possible from thawing of the Arctic permafrost, a priority of future satellite-based measurements of CH_4 of this region would be very valuable.

- ***Carbon dioxide – CO_2:*** In 2008 the mixing ratios of CO_2 reached **new record levels** both globally and at Zeppelin. The global mean value for 2008 was 385.2 ppb (WMO, 2008), after an increase of 2.0 ppm from 2007. The mean annual increase during the last 10 years is 1.93 ppm. The observations of CO_2 are performed by the University of Stockholm. As their final 2008 analysis is not yet completed, only preliminary results are shown in this report.

- ***Hydrofluorocarbons:*** These gases have replaced ozone depleting substances, and are relatively new gases emitted to the atmosphere. They are all of solely anthropogenic origin.

The mixing ratios of HFC-125, HFC-134a, HFC-152a have **increased by as much as 249%, 159% and 207% respectively since 2001** at the Zeppelin observatory. However, their concentrations are still very low, so the total radiative forcing of these gases since the start of their emissions and up to 2008 is only about 0.01 W m^{-2}. Thus the contribution from these manmade gases to the global warming is currently considered small. Given the observed extremely rapid increase in the concentrations it is still crucial to follow the development of these gases in the future.

- ***The perfluorinated compound – SF_6:*** The only perfluorinated compound measured at Zeppelin is Sulphurhexacloride, SF_6. This is an **extremely potent greenhouse gas,** but the concentration is still very low. However, measurements show that the concentration has increased by as much as 33% 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 all greenhouse gases. The amount of most of the ozone-depleting substances (ODS) in the troposphere is now declining slowly globally and is expected to be back to pre-1980 levels around the year 2050. The gases included in the monitoring programme at Zeppelin 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 give reason for optimism. The concentrations of the observed CFCs, **CFC-11, CFC-12, CFC-113 and CFC-115 are all declining**. The mixing ratios of three of the four gases are now at a lower level than in 2001 when we started the measurements. For the compound CFC-115 the increase has slowed down and we expect the trend for 2001–2009 to be negative. The climate forcing of this compound is negative from 2004.

- ***HCFCs:*** The CFC substitutes HCFC-22, HCFC-141b and HCFC-142b all had a relatively strong increase in the levels measured at Zeppelin from 2001-2008. HCFC-22 used for temperature control and foam blowing had the largest growth rate. This is the most abundant substance of the HCFCs and is currently increasing at a rate of 6.2 ppt/year which is more than 3% per year. **HCFC-142b had the strongest relative increase with more than 8% since 2007 and more than 40% since 2001.**

- ***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 not regulated through the protocols – Key findings

The monitoring programme also includes five greenhouse gases not regulated through any of the two protocols.

- ***Chlorinated greenhouse gases:*** These are the following chlorinated gases: Methylchloride (CH_3Cl), Dichloromethane (CH_2Cl_2), Chloroform ($CHCl_3$), Trichloromethane (C_2HCl_3), Perchloroethylene (C_2Cl_4). **The levels of all these gases have decreased the last years except for Dichloromethane.** Dichloromethane show an increase of more than 20% since 2001, and as much as 8% the last year**.** The main use of this compound is that it is an active ingredient in paint removers.

Long range transport of pollutions; aerosols and reactive gases – Key findings

- ***Aerosols:*** Aerosols are atmospheric small particles. Observations of the total amount of aerosols above Ny-Ålesund and Zeppelin show increased aerosol levels during spring time compared to the rest of the year. This is expected and is called Arctic haze which is due to transport of pollution from lower latitudes (mainly Europe and Russia) during winter/spring in combination with inversion. In 2008 this aerosol pollution was at approximate the same level as previous years. There were shorter episodes with elevated levels of aerosols later, particularly in May. Aerosols are short-lived climate forcing agents and an extension of the aerosol observations at Zeppelin by including measurements of the aerosol absorption properties will be very useful to improve the knowledge of the aerosol type and their effects in the Arctic atmosphere.

- ***Reactive gases:*** Tropospheric ozone and CO have elevated levels in polluted regions like central Europe. They are suitable indicators for long range transport of pollution from the continents to Svalbard, and CO is also a proper tracer for transport of emissions from biomass burning events. There are several episodes with elevated levels of ozone and CO in 2008 indicating long range transport, but none episode as extreme as the one in 2006. In general there has been **a reduction in the CO concentration the last years at Zeppelin, but an increase from 2007–2008**. The explanation to this is not yet understood. The annual mean value for 2008 was 123 ppb which is ~1.5% higher than for 2007.

- ***Episodes of long range transport:*** In 2008 there were several episodes with polluted air transported to Zeppelin, and strong episodes particularly in January and May resulted in elevated levels of CH_4, CO, and CO_2. However, **it is important to emphasise the high frequency of days in 2008 with air arriving at Zeppelin that has only been circulating within the Arctic region**. Particularly the last 2 years there has been fewer episodes with long range transport from Europe and Russia reaching the observatory. This means that the observations at Zeppelin might seem to be less influenced by long range transport of pollution from central Europe in 2007 and 2008, than the years 2004 and 2005.

2. Introduction

The greenhouse effect is a naturally occurring process in the atmosphere caused by trace gases, especially water vapour (H_2O), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) 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 is approximately 13.7 ^{o}C,, more than 30 degrees higher than it would have been without these gases present (IPCC, 2007). This is the natural greenhouse effect. The enhanced greenhouse effect refers to the additional effect of the greenhouse gases from human activities. In the industrial era, after 1750, the concentration of greenhouse gases in the atmosphere has increased significantly. The global atmospheric mean mixing ratios of CO_2 has increased by 38% (from 280 ppm as a pre-industrial concentration to 385.2 ppm in 2008) and methane has increased by as much as 157% from 700 ppb to 1789 ppb in 2008) according to WMO (WMO, 2009). 2008 showed new record levels of both these gases. The overall changes in the concentrations of the greenhouse gases are the main cause of the global mean temperature rise of 0.74^{o}C over the last century reported by IPCC (2007). Depending on the various emission scenarios used the temperature will continue to increase with 1.1-6.4 ^{o}C approaching the year 2100, according to IPCC (2007).

Radiative forcing[1] 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 4th IPCC assessment report 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.

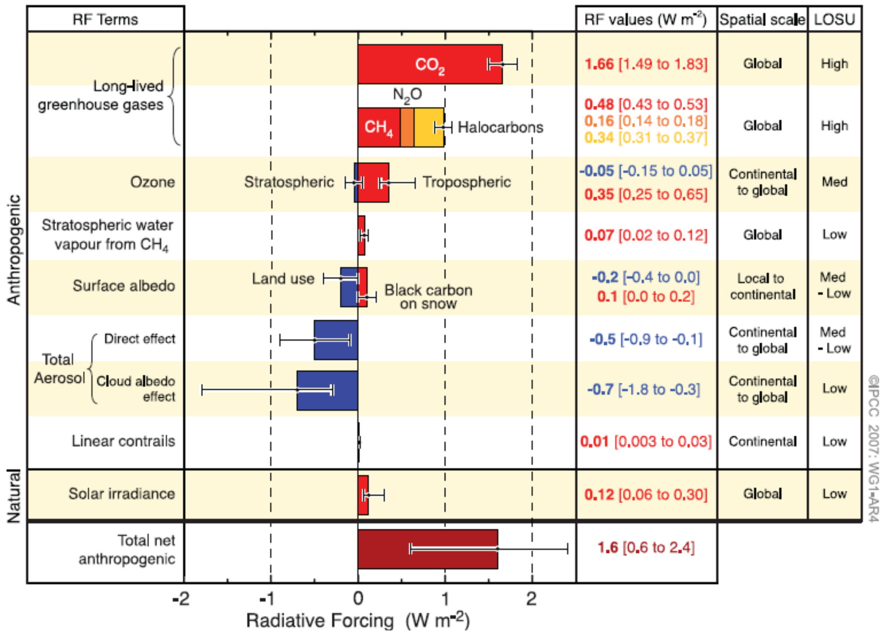

Figure 1: *Global-average radiative forcing (RF) estimates for important anthropogenic agents and mechanisms together with the typical spatial scale of the forcing and the assessed level of scientific understanding (LOSU).*

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[1] 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^{-2} 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^{-2} given in the 4th IPCC report (IPCC, 2007). This is an increase of 0.2 W m^{-2} since the IPCC report from 2001. CH_4 and N_2O are other components with strong forcings of 0.48 W m^{-2} and 0.16 W m^{-2} 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_2O, 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_6. These fluorinated gases are regulated through the Kyoto protocol. The total forcing of the halocarbons is 0.337 Wm^{-2}, and the single component CFC-12 is presently stronger than N_2O, 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.

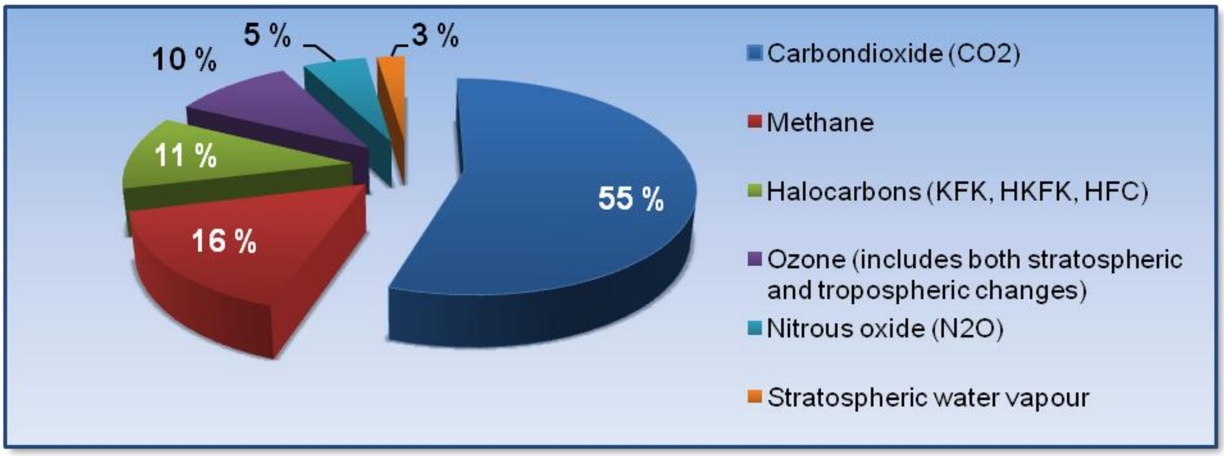

Figure 2: The relative contribution in percent of the long-lived greenhouse gases and ozone to the anthropogenic warming since pre-industrial times (1750). The numbers are based on the radiative forcing estimates in the last IPCC report.

The main objective of NILU’s monitoring programme on Svalbard is to observe, analyse and interpret the changes in the gases included in 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 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 an 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, SF_6 (sulphur hexafluoride), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). 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.

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 of CO_2, 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 the trend for each component is given. The acceleration in the trend indicates how the growth rate is expected to change in the coming years[2], assuming the same development in the emissions.

Table 2: Yearly average concentration levels of greenhouse gases measured at the Zeppelin station for the years 2001-2008. All concentrations are in ppt$_v$, except for methane and carbon monoxide (ppb$_v$) and CO_2 (ppm$_v$). The trends are calculated from observations for the period 2001-2008.

Compound	**Formula**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**Trend / year**	**Change in trend**
Methane	CH_4	1858	1853	1870	1859	1863	1865	1877	1884	+4.1	+1.64
Carbon monoxide	CO		125.9	141.5	132.9	132.6	125.6	120.9	122.9	-1.7	0.75
Carbon dioxide[*]	CO_2	371	373	376	378	381	382	384	NA	+ 2.3*	-0.29*
Chlorofluorocarbons											
CFC-11	$CFCl_3$	263	264	263	260	259	256	249	244	-2.8	-1.15
CFC-12	CF_2Cl_2	549	561	563	562	560	558	546	538	-2.1	-3.2
CFC-113	$CF_2ClCFCl_2$	81.6	82.6	82.6	81.9	81.1	79.6	78.1	76.7	-0.79	-0.40
CFC-115	CF_3CF_2Cl	8.3	8.5	8.5	8.6	8.6	8.5	8.5	8.4	+0.01	-0.000
Hydrochlorofluorocarbons											
HCFC-22	CHF_2Cl	161	171	180	183	188	195	200	208	+ 6.23	-0.31
HCFC-141b	CH_3CFCl_2	16.6	18.1	19.0	19.5	19.6	19.9	20.3	21.1	+ 0.55	-0.137
HCFC-142b	CH_3CF_2Cl	14.9	15.7	16.4	17.0	17.7	18.8	19.6	21.1	+ 0.84	+0.01
Hydrofluorocarbons											
HFC-125	CHF_2CF_3	2.0	2.6	3.2	3.8	4.4	5.1	5.9	6.9	+0.69	+0.06
HFC-134a	CH_2FCF_3	20.7	26.1	31.0	35.7	40.1	44.3	48.6	53.8	+4.62	-0.11
HFC-152a	CH_3CHF_2	2.9	3.5	4.1	4.9	5.6	6.7	7.7	8.8	+0.83	+0.08
Halons											
H-1301	CF_3Br	3.0	3.1	3.2	3.2	3.3	3.4	3.3	3.3	+ 0.04	-0.03
H-1211	CF_2ClBr	4.4	4.5	4.6	4.7	4.7	4.6	4.5	4.4	+ 0.00	-0.05
Halogenated compounds											
Methyl Chloride	CH_3Cl	507	525	530	525	521	521	520	523	+0.9	-1.7
Methyl Bromide	CH_3Br	9.3	9.1	8.8	8.9	8.7	8.9	8.7	8.2	-0.10	-0.01
Dichloromethane	CH_2Cl_2	31.0	31.5	32.9	32.7	32.1	33.5	35.3	37.8	+0.84	+ 0.28
Chloroform	$CHCl_3$	10.9	10.7	10.8	10.5	10.5	10.5	10.6	10.4	-0.04	+0.02
Trichloromethane	CH_3CCl_3	37.6	32.4	27.6	23.0	19.2	16.0	13.3	11.0	-3.83	+0.53
TriChloroethylene	$CHClCCl_2$	0.6	0.6	0.5	0.5	0.3	0.4	0.3	0.4	-0.03	0.04
Perchloroethylene	CCl_2CCl_2	4.1	4.0	4.0	3.9	3.1	2.7	2.9	2.7	-0.24	+0.06
Sulphurhexafluoride	SF_6	5.0	5.1	5.3	5.6	5.7	6.1	6.3	6.6	+0.2	+0.02

[*] _Measurements of Carbon dioxide are performed by Stockholm University, Department of Applied Environmental Science (ITM). The results for 2008 are not available (NA) yet, the trend and change in trend is for the period 2001-2007._

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[2] 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. The ozone depleting 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. Zeppelin observatory is a unique site for observations of changes in the background level of atmospheric components. All peak concentrations of the measured gases are significantly lower at Ny-Ålesund than at other sites, due to the stations remote 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, Carbon Monoxide and tropospheric ozone) 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 dependant on the solar intensity.

3.1.1 Observations of methane in the period 2001-2008

Methane (CH_4) is the second most important greenhouse gas after CO_2 with a radiative forcing of 0.48 W m^{-2} since 1750 and up to 2005. In addition to be a dominating greenhouse gas, methane also plays a significant role in the atmospheric chemistry. In the atmosphere 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 is responsible for the cleaning of the atmosphere. Increased levels of methane might lower the concentration of OH, influencing the levels of other compounds as well. 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 mixing ratio has been relatively stable over the period 1998-2005. The global average change was close to zero for this period according to IPCC (Forster et al, 2007), and also at our site for the short period 2001-2004. 2003 was an exception globally and at Zeppelin; a maximum annual mean of 1870 ppb at Zeppelin was obtained, considerable higher that the other years. Recently an increase in the methane levels is evident from our observations, and also observations at other sites (Rigby et al, 2008; WMO, 2009). Figure 3 presents the observations of methane at Zeppelin since the start in 2001.

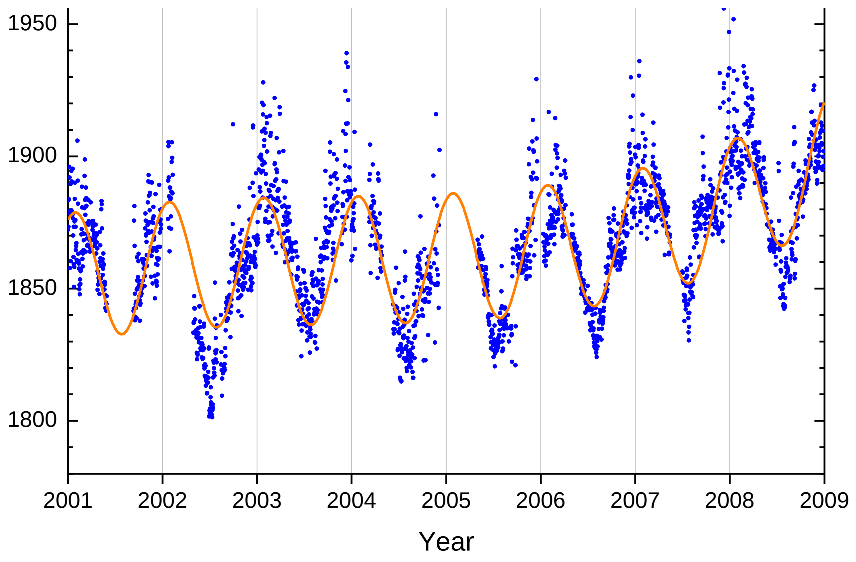

Figure 3: Observations of daily averaged methane concentrations for the period 2001-2008 at the Zeppelin observatory. Blue dots: observations, orange solid line: modelled background methane mixing ratio.

As can be seen from Figure 3 there is an increase in the concentrations of methane observed at Zeppelin the last years. The pronounced increase started in November/December 2006 and continues throughout the year 2007 and 2008, and is particularly evident in the late summer-winter 2007. A maximum methane mixing ratio as high as 1956 ppb was observed 10th December 2007. This was 2.9% above the background value, and the highest value ever recorded at Zeppelin. There were values nearly as high as this in 2008. The strongest episodes in 2008 were on the 16th January and 6th September with methane observations 2.4% and 2% above the background values, respectively. Analyses of source regions for the episodes are included in section 5 on 44.

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 Figure 3. 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 +4.1 ppb_v per year for the period 2001-2008 this corresponds to an increase of 0.17% per year. Comparably the annual trend for the period 2001-2007 was +2.7 ppb_v thus the last year increase has changed this substantially. The acceleration in the trend is positive, 1.64 in 2008, even more positive than last year (+1.2) (see Table 2). This indicates that the trend per year can be expected to continue to increase in the coming years, if the same processes continue to regulate the methane level. Although, this assumption is connected with large uncertainty as the reason for the observed increase is not clear and additionally, the seasonal and annual variations are large and the time series 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 2001-2008. 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.

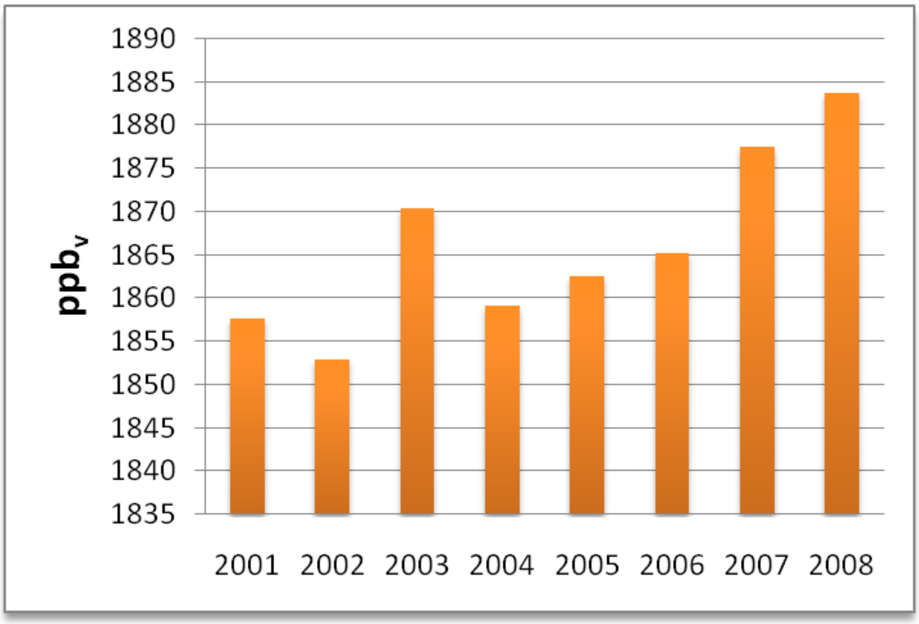

Figure 4: Development of the annual mean mixing ratio of methane measured at the Zeppelin Observatory for the period 2001-2008.

This diagram clearly illustrates the large increase in the concentrations of methane the last years, with 2008 as a new record year. The annual mean mixing ratio for 2008 was 1884 ppb$_v$ while the level was 1877 ppb$_v$ in 2007. This is an increase of 0.34%, the last year which is weaker than from 2006-2007 when the increase was as high as 12 ppb (0.64%). The increase since 2004 is more than 1.3 % which is considered as relatively large compared to the development of the methane mixing ratio in the period from 1999-2005. (All annual means are included in Table 2 on page 14).

Also stations at other locations show a significant increase in methane for the year 2007 and 2008, at both hemispheres. According to WMO (WMO, 2009) there has been a global increase in the methane concentration by 0.34% from 2006 to 2007 and a continuation of the increase up to a new record level in 2008, 0.39% above the 2007 level. Thus the global increase is slightly higher than what we observed at Zeppelin for 2008. This might be due to a delay in the mixing between northern and southern hemisphere after the large increase from 2006-2007 at the northern latitudes.

For 2007, Rigby and his co-workers report a global increase of methane (Rigby et al, 2008). They have analyzed methane observations from 12 sites worldwide, and found an increase of around 10 ppb$_v$ at all sites since 2006. The largest increase was observed at Mace Head in Ireland and Alert. Alert is a site north in Canada (82 ^{o}N), and the site closest to the Zeppelin observatory at Svalbard, but interestingly they also found a large increase at sites at low latitudes e.g. in California and Ragged Point, Barbados.

The average CH_4 concentration in the atmosphere is determined by a balance between emission from the various sources at the earth's surface and reaction and removal 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, rice paddies, emissions from ruminant animals, biomass burning, and fossil fuels combustion. Further, methane is the principal component of natural gas and e.g. leakage from pipelines, off-shore and on-shore installations are known source of atmospheric methane. The distribution between natural and anthropogenic sources is approximately 40% natural sources, and 60% of the sources are direct a result of anthropogenic emissions. Of natural sources there is a large unknown amount of methane in methane clathrates (so called methane hydrates) at 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 feedback 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^oC since 1980s.

Currently the observed increase the last years 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 level observed in 2003 is a global feature, and is still not fully understood. It is essential to find out if the increase is due to large point emissions or if it is newly initiated processes releasing methane to the atmosphere like e.g. the melting of the permafrost layer. Recent and ongoing scientific discussions point in the direction of increased emissions from wetlands located both in the tropical region (in 2006) and in the Arctic region.

We have performed an analysis and assessment of the source regions of the air arriving at Zeppelin in the period 2001-2008 as described in section 5 at page 44.The most striking result of this analysis is that in 2007 and 2008 the fraction of air arriving at Zeppelin categorized as clean marine and Arctic air was clearly higher than 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.

3.1.2 Observations of Carbon Dioxide (CO_2) in the period 1988-2007

CO_2 is the most important greenhouse gases with a radiative forcing of 1.66 W m^{-2} since 1750 and an increase in the forcing of as much as 0.2 W m^{-2} since the IPCC report from 2001 (Forster et al., 2007). CO_2 is the end product in the atmosphere of the oxidation of all main organic compounds and has shown an increase of as much as 38 % since the pre industrial time (WMO, 2009).

The atmospheric CO_2 concentration measured at Zeppelin Observatory for the period 2001-2008 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.

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 1988-2008 shown.

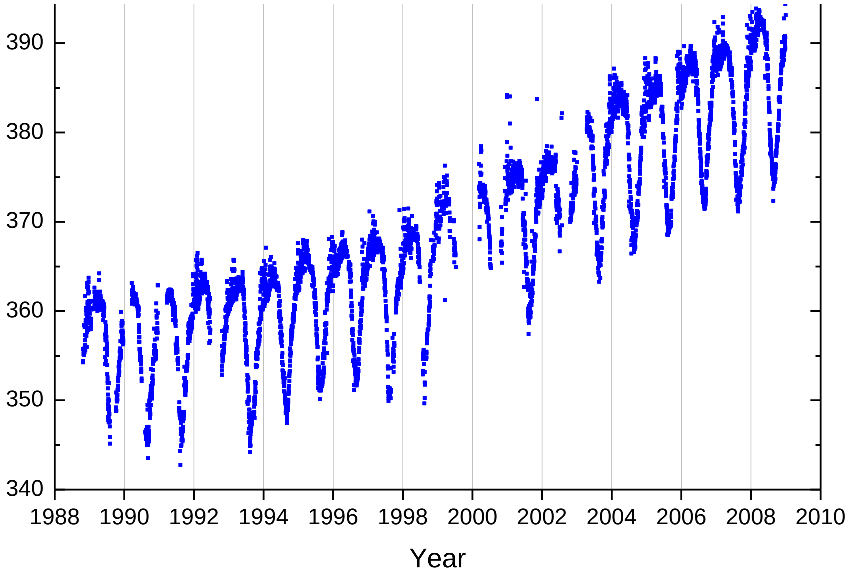

Figure 5: The CO_2 concentration measured at Zeppelin Observatory for the period 2001-2008.

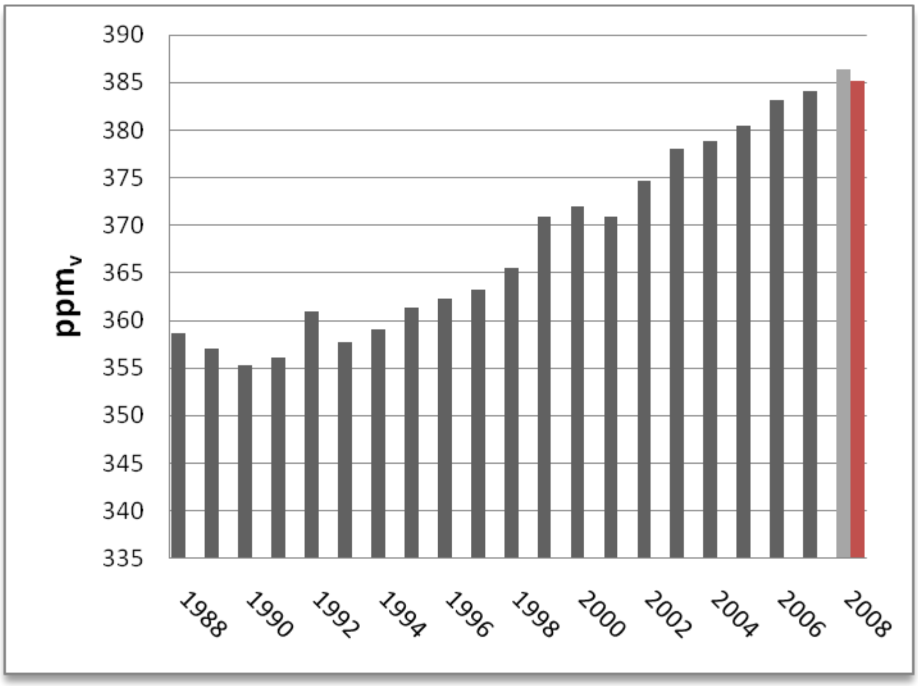

Figure 6: Development of the annual mean mixing ratio of CO_2 measured at Zeppelin observatory for the period 1988-2008.The light grey bar is the preliminary results for 2008, the red bar shows the global annual mean for 2008 (WMO, 2009).

The results show that 2008 is a new record year for the annual mixing ratio of CO_2 at Zeppelin. Unfortunately ITM University of Stockholm have not completed their analysis of the observations yet, thus the mean value for 2008 is preliminary, and not published in this report. It is shown as a light grey bar in the Figure. The preliminary results indicate that there is an increase of 0.6% since 2007. The global mean value for 2008 is 385.2 ppb (WMO, 2009). This is an increase of 0.52% (2.1 ppb) since 2007 and the mean global annual increase is 1.93 ppb the last 10 years. The main reason why the CO_2 level is higher at Zeppelin than globally is that in general the CO_2 emissions are lower in the Southern hemisphere, and the global mixing takes a certain time.

A more detailed analysis of the CO_2 results 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 2001-2008

Methyl chloride (CH_3Cl) is the most abundant halocarbon in the atmosphere. The main sources of Methyl Chloride in the atmosphere are natural and dominating source is thought to be the algae in the ocean, with biomass burning as the second largest source. But also emissions from warm coastal land, particularly from tropical islands are shown to be a significant source. Due to the dominating natural sources, this compound is not regulated trough any of the Montreal or Kyoto protocols, but is an important natural source of Chlorine to the stratosphere.

The results of the observation of this substance for the period 2001-2008 are shown in Figure 7.

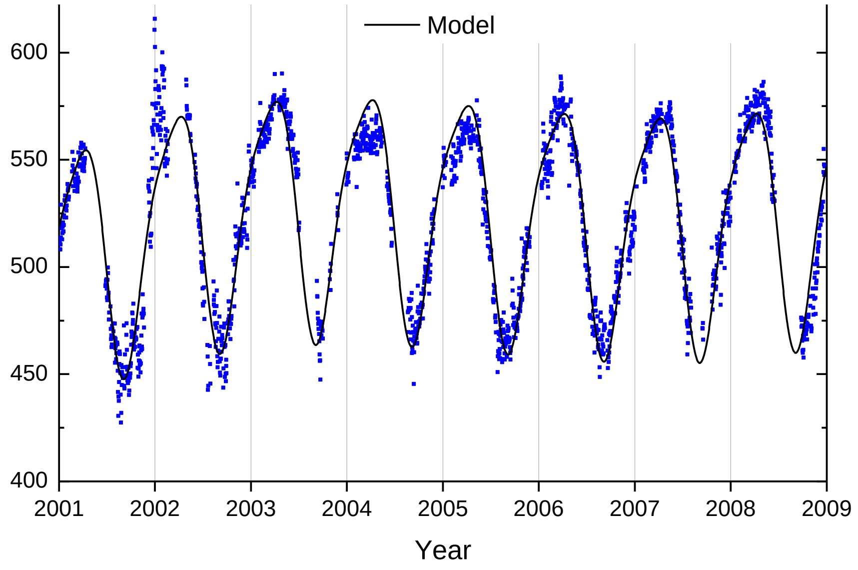

Figure 7: Observations of methyl chloride, CH_3Cl, for the period 2001-2008 at the Zeppelin observatory. Dots: daily averaged concentrations from the observations, solid line: modelled background mixing ratio.

The lifetime of the compound is only 1.3 year resulting in large seasonal fluctuations as shown in the Figure. Thus 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 contributes to the stratospheric Chlorine burden. With respect to the warming potential this substance is 16 times stronger than CO_2 per kg gas emitted.

By use of the model described in Appendix I we have calculated the annual trend, and the change in the trend is also given in Table 2. The trend for the period 2001-2008 is 0.9 ppt per year, and the change in the trend is -1.7, indicating a slowdown in the annual change.

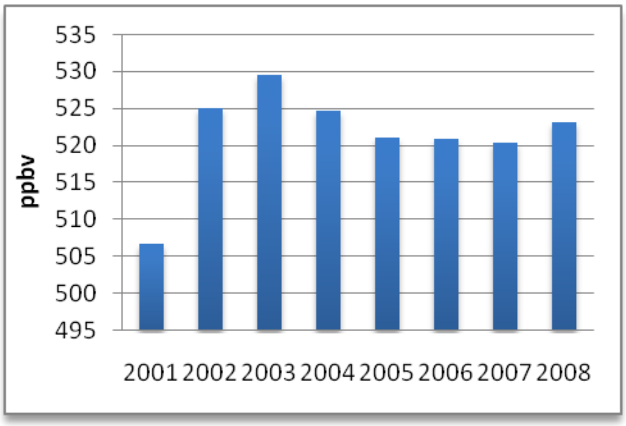

Figure 8: Development of the annual means methyl chloride measured at the Zeppelin Observatory for the period 2001-2008.

The development of the annual means of methyl chloride for the period 2001-2008 is presented in Figure 8. The last years there has been a stabilisation of the level of this gas, but from 2007-2008 there is an increase of 0.5%. As one of the main sources of this compound is algae from the ocean, it is interesting to note the development the last years as the sources might be indirectly related to sea ice cover in the Arctic region, and thus also to the temperatures in the region.

3.1.4 Observations of Methyl Bromide in the period 2001-2008

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 2001-2008 are shown in Figure 9.

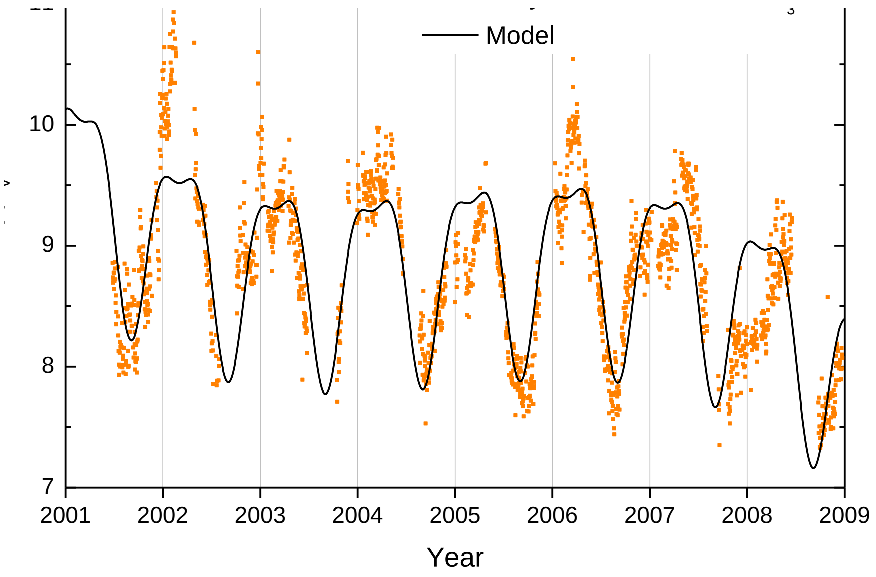

Figure 9: Observations of methyl bromide, CH_3Br, for the period 2001-2008 at the Zeppelin observatory. Dots: daily averages mixing ratios from the observations, solid line: modelled background mixing ratio.

Methyl bromide is a greenhouse gas with a lifetime of 0.7 years and it is 5 times stronger than CO_2, if the amount emitted of both gases were equal. The short life time explains the large annual and seasonal variations of this compound. While methyl bromide is a natural substance, the additional methyl bromide added to the atmosphere by humans contributes to the man made 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 31.

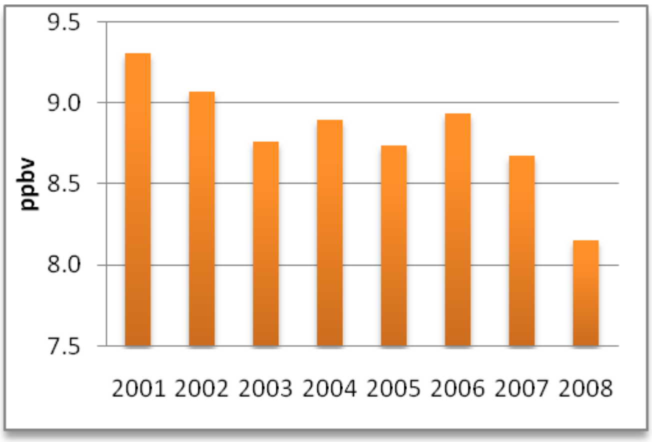

Figure 10: Development of the annual means of Methyl Bromide measured at the Zeppelin Observatory for the period 2001-2008.

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 2001-2008 there is a reduction in the mixing ratio of -0.1 ppt per year, with a very small acceleration in the trend of -0.01 indicating that the trend is expected to be similar, or slightly lower, for the next year (if there are no abrupt changes in sources and sinks). However, note that the observed changes are small and the daily, seasonal and annual variations of the trends are uncertain.

The development of the annual means for the period 2001-2008 is presented in Figure 10, clearly illustrating the decrease the last years. In general atmospheric amounts of methyl bromide have declined since the 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^{-2} (IPCC, 2007) due to changes in the concentrations since 1750. This is 10% of the overall global radiative forcing since 1750. There are no direct anthropogenic sources for ozone; thus the component is not regulated by the Kyoto protocol. Ozone is not emitted directly to the atmosphere, but 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 µg/m3 for hourly mean, 60 µg/m3 for eight-hour mean and 50 µg/m3 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 2001-2008 are shown in the next Figure.

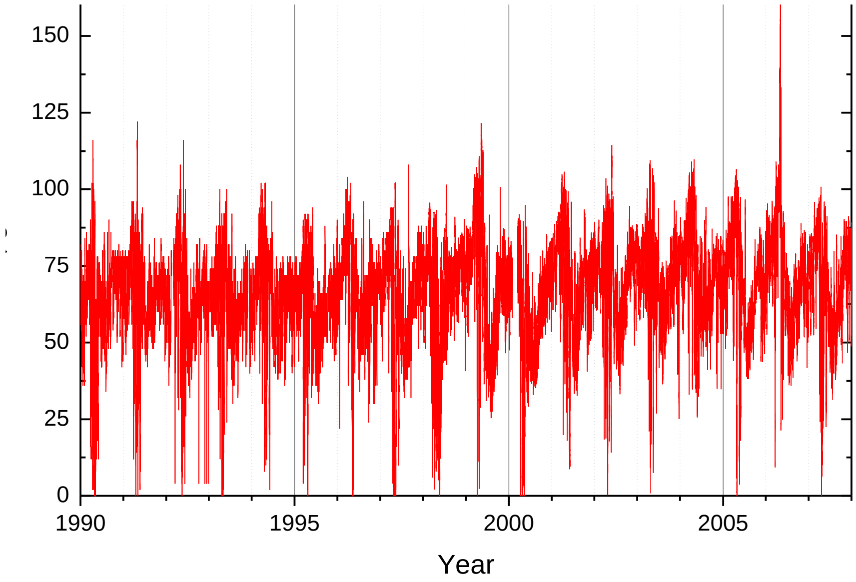

Figure 11: Observations of ozone in the troposphere for the period 2001 to 31.07.2008 at the Zeppelin observatory. Red dots: hourly average concentrations.

Monthly mean concentrations show large seasonal variations. In 2006 there was an extreme episode with transport of pollution into the Arctic region and ozone levels as high as ~160 µg m^{-3}. This was above all critical levels. In 2008 there have been few strong episodes, and the maximum ozone level observed was 109 µg m^{-3} at 21th of May 2008.

3.1.6 Observations of CO in the period 2001-2008

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 level of methane and production tropospheric ozone which are both very important climate 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; CO plays a key role in the control of the OH radical.

The observed CO mixing ratio for the period September 2001-2008 are shown in Figure 5.

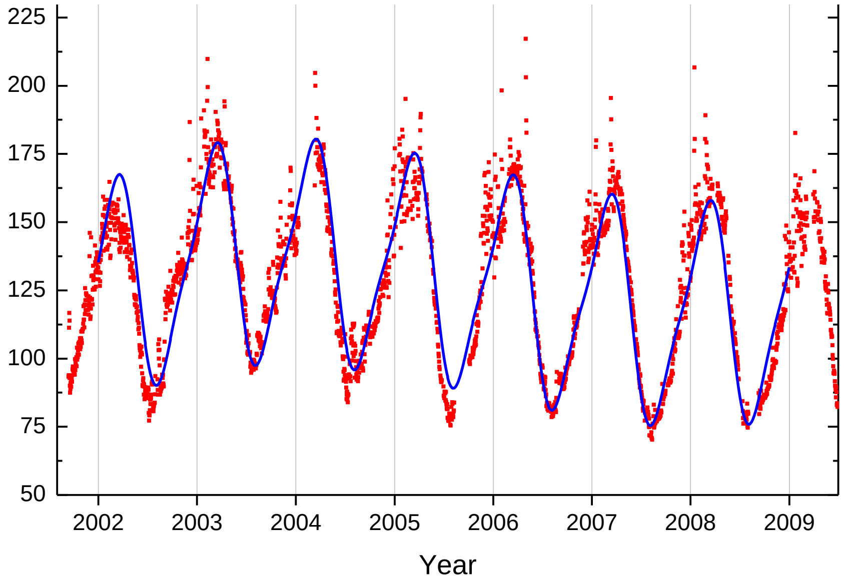

Figure 12: Observations of carbon monoxide (CO) for the September 2001 to July 2009 at the Zeppelin observatory. Red dots: daily averaged observed mixing ratios. The solid: line is the modelled background mixing ratio.

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.

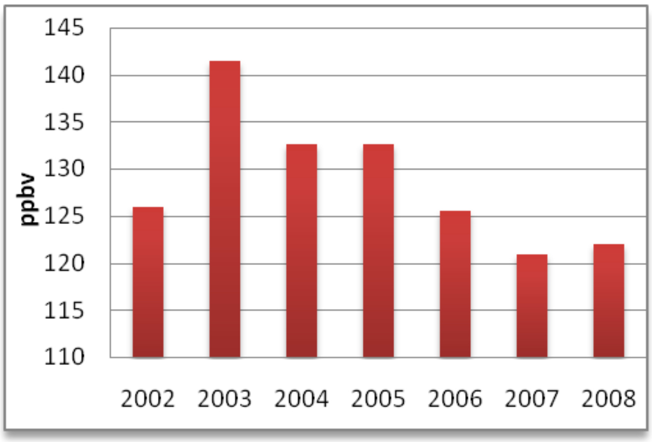

Figure 13: Development of the annual means of CO measured at the Zeppelin Observatory for the period 2001-2008.

The maximum daily average value in 2008 was observed on the 16th of January and was 206.6 ppb. This is the third highest concentration ever observed at Zeppelin; the highest is 217.2 ppb on the 2nd of May 2006. These peak values are due to transport of polluted air from lower latitudes, and for CO it is often caused by transport of smoke from agricultural fires or forest fires. In general the CO concentrations measured at Zeppelin show a decrease during the period and 2007 is the minimum for the period investigated. The decrease in the background mixing ratio of CO is as much as 13% from 2003 to 2007. However, in 2008 there is an increase of 1.6% since 2007. This is important to monitor, as the sources of CO are both several and complex, and the level of this compound is important for the ozone and methane levels. 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.

The global levels of CO were increasing before mid-1980s, and the averaged global growth rate was -0.9 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 -1.7 ppb per year for the period 2002-2008. The development of the annual means for the period 2002-2008 is presented in Figure 13, clearly illustrating a maximum in the year of 2003, and a decrease from 2003-2007, with an increase the last year.

3.2 Greenhouse gases with solely anthropogenic sources

All the gases presented in this chapter have solely anthropogenic sources. These are the man-made greenhouse gases and are called CFCs, HCFCs, HFCs PFCs, SF_6 and halons and the gases did not exist in the atmosphere before the 20th century. All these gases except for SF_6 are halogenated hydrocarbons. 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. Together as a group the gases contribute 11% to the overall global radiative forcing since 1750.

Some of these gases are ozone depleting, and consequently regulated through the Montreal protocol. Additional chlorine and bromine from CFCs, HCFCs and halons 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, around the year 2000, and observations until 2004 confirm that the level of stratospheric chorine has not continued to increase (WMO, 2007).

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).

There are 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 comprises the components called HCFCs listed 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 2001-2008

This section include 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.

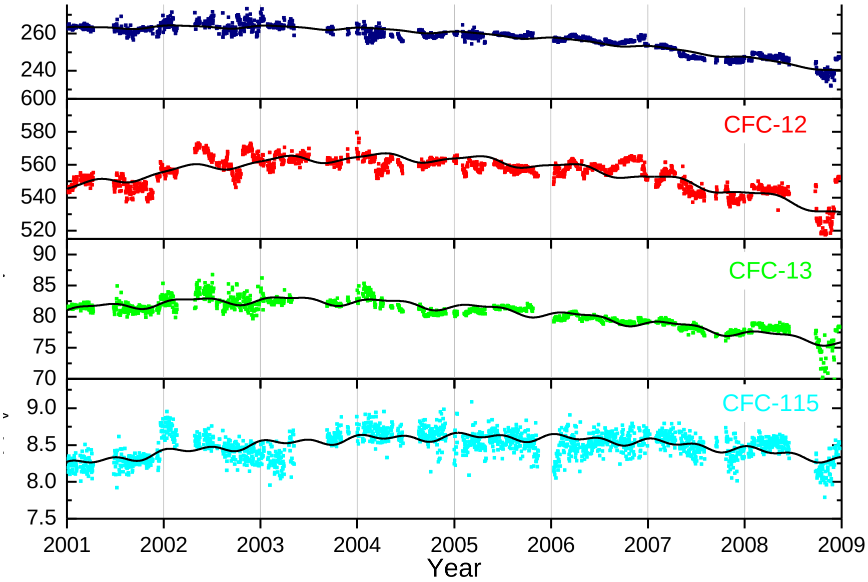

Figure 14: Daily averaged mixing ratios of the monitored CFCs: CFC-11 (dark blue), CFC-12 (red), CFC-13 (green) and CFC-115 (light blue) for the period 2001-2008 at the Zeppelin observatory. The solid lines are modelled background mixing ratio.

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 and maximum emissions was around 1987. 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 very 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, and the changes in the trends are also negative indicating acceleration in the decline. For the compound CFC-115 the trend is still slightly positive, +0.01 ppt/year, but the change in trend is negative and thus we expect the trend for 2001-2009 to be negative. In total the development of the CFC levels at the global background site Zeppelin is now very promising.

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 at Zeppelin for the period 2001-2008 (-0.79 ppt/yr for 2001-2008), but we find a larger reduction for CFC-11, approximately 2.8 ppt/year. In Europe the growth rates for CFC-11 was -2.7 for 2003-2004, in agreement with our results. The difference might be explained by the distribution of the sources, and the very remote location of the Zeppelin observatory.

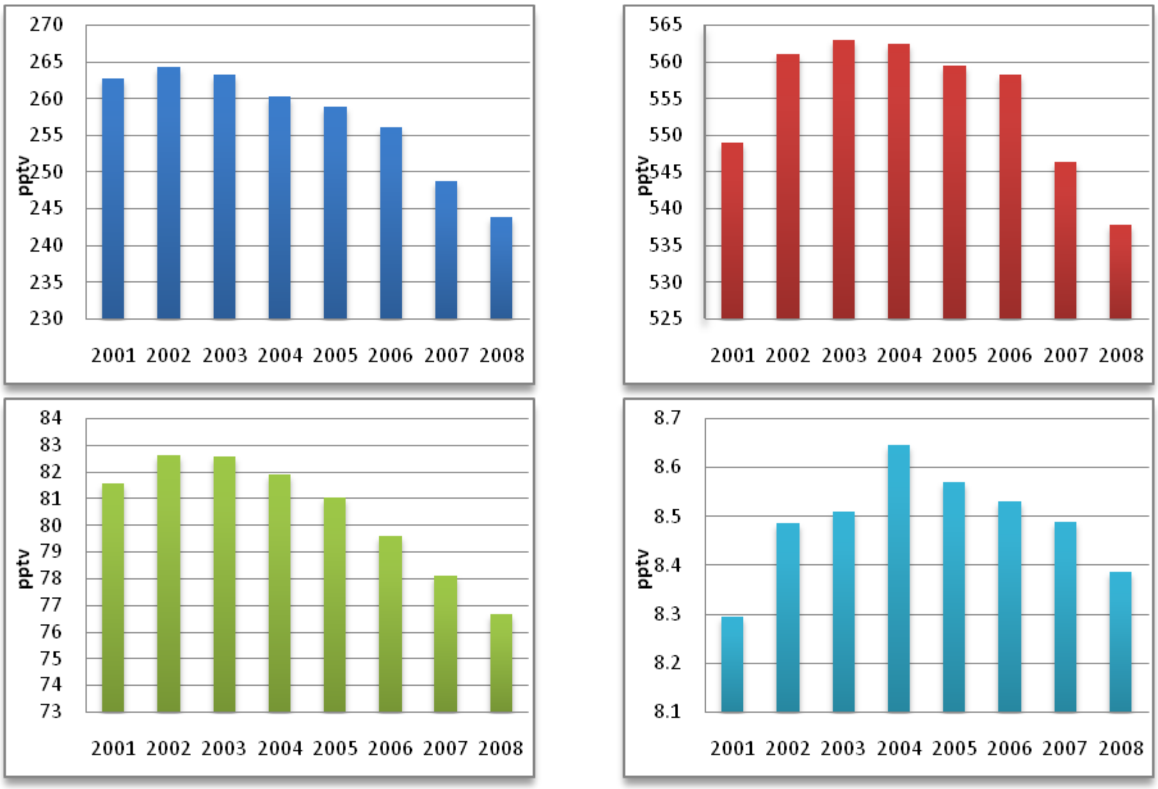

Figure 15: Development of the annual means all the observed CFCs at the Zeppelin Observatory for the period 2001-2008. Upper left panel: CFC-11, upper right panel: CFC-12, lower left panel: CFC-13, lower right panel: CFC-115.

The development of the annual means for all the observed CFCs is shown in Figure 15, and it 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 (the red diagram) 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 gas has 10600 times stronger warming effect than 1 kg emitted CO_2 gas. The global averaged atmospheric mixing ratio of CFC-12 has 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 has the maximum in 2003-2004, but the variations since 2001 is larger than the global average variation.

3.2.2 Observations of Hydrochlorofluorocarbons (HCFCs) in the period 2001-2008

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, 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 2001-2008.

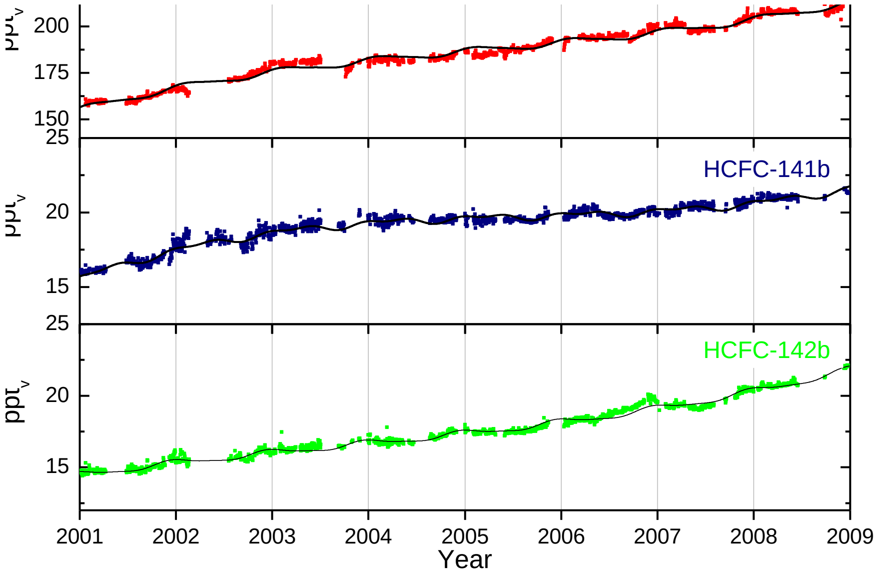

Figure 16: Daily average mixing ratios of the monitored HCFCs: HCFC-22 (red), HCFC-141b (dark blue) HCFC-142b (green) for the period 2001-2008 at the Zeppelin observatory. The solid lines are modelled background mixing ratio.

The trends per year for the compounds HCFC-22, HCFC-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 6.2 ppt/year. In comparison, the global mean increase for 2000-2004 was +4.9 ppt/year according to WMO, (WMO, 2007). The mixing ratios of HCFC-141b and HCFC-142b have 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 lower than projected in the previous Ozone Assessment (WMO, 2007).

The Figure 17 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.

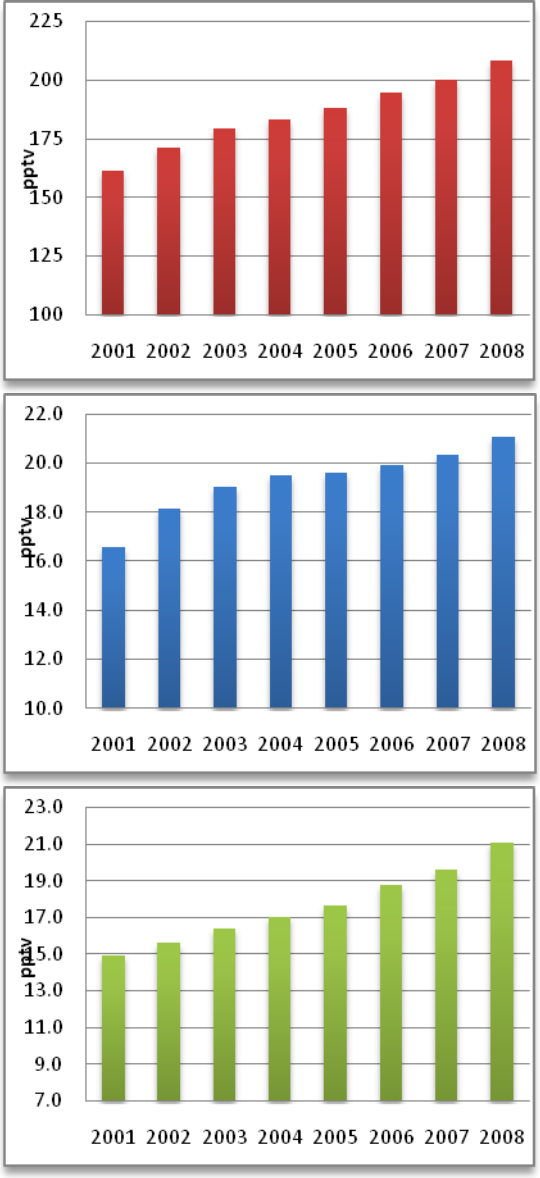

Figure 17: Development of the annual means the observed HCFCs at the Zeppelin Observatory for the period 2001-2008. Red: HCFC-22, Blue: HCFC-141b, and green: HCFC-142b.

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 use of the gases is now frozen, but they are 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 2001-2008

The substances called HFCs are the so called second generation replacements of CFCs, which means that they are considered as better alternatives to the CFCs with respect to the ozone layer than HCFCs described in the previous section. 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 chlorine thus they do not have a direct influence on the ozone layer, but they are infrared absorbers and contribute to the global warming.

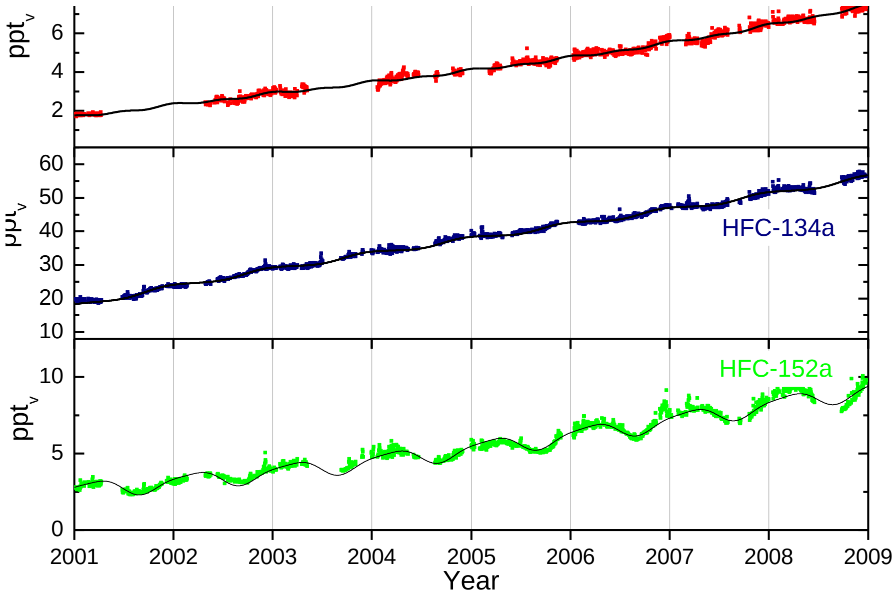

Figure 18: Daily average concentrations of the monitored CFCs: HFC-125 (red), HFC-134a (dark blue), HFC-152a (green) for the period 2001-2008 at the Zeppelin observatory. The solid lines are modelled background mixing ratio.

HFC-152a has the shortest 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.

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. Still their mixing ratios are rather low, but the background mixing ratios are increasing steeply as our results show. This is also clearly illustrated in Figure 19 showing the development of the annual means. The gases are continuously increasing at a constant rate per year as earlier.

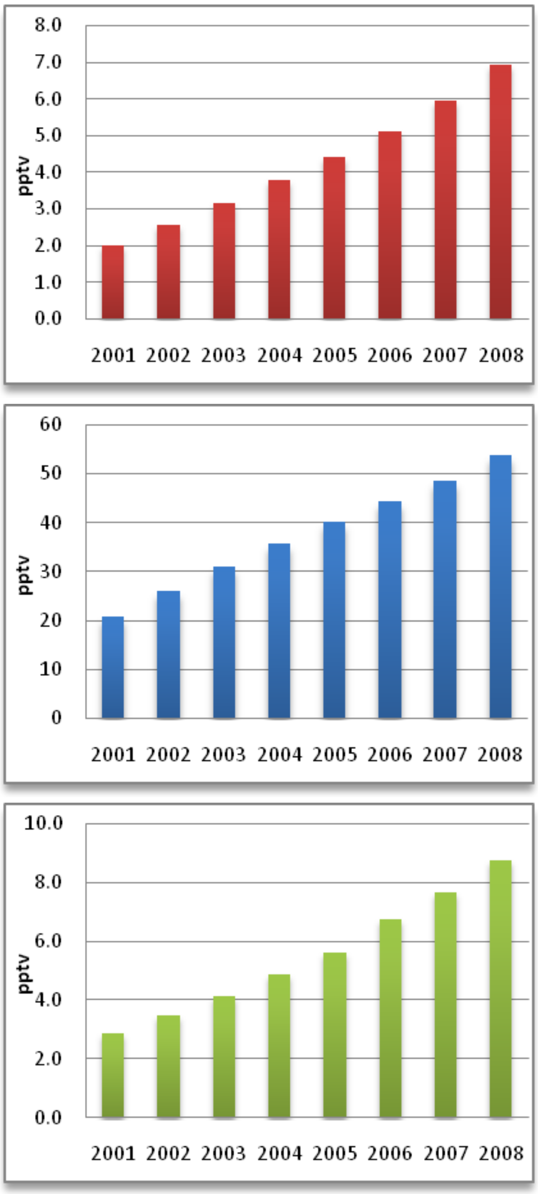

Figure 19: Development of the annual means the observed HFCs at the Zeppelin Observatory for the period 2001-2008. Red: HFC-125, Blue: HFC-134a, and green: HFC-152a.

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 2001-2008 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 halocarbons observed at Zeppelin. The mixing ratios of HFC-125, HFC-134a, HFC-152a has increased by as much as 249%, 159% and 207% 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 emissions of these gases since the start of the emissions is 0.01 W m^{-2} for these three gases. Thus the contribution from the recent man made emissions of these gases is still considered as small. This is explained by the (still) low mixing ratios of the compounds.

3.2.4 Observations of Halons in the period 2001-2008

Halons include the following components: H-1301, H-1211. These climate gases contain bromine, also contribution to the depletion of the ozone layer. Actually, bromine is even more effective in destroying ozone than chlorine. The halons 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.

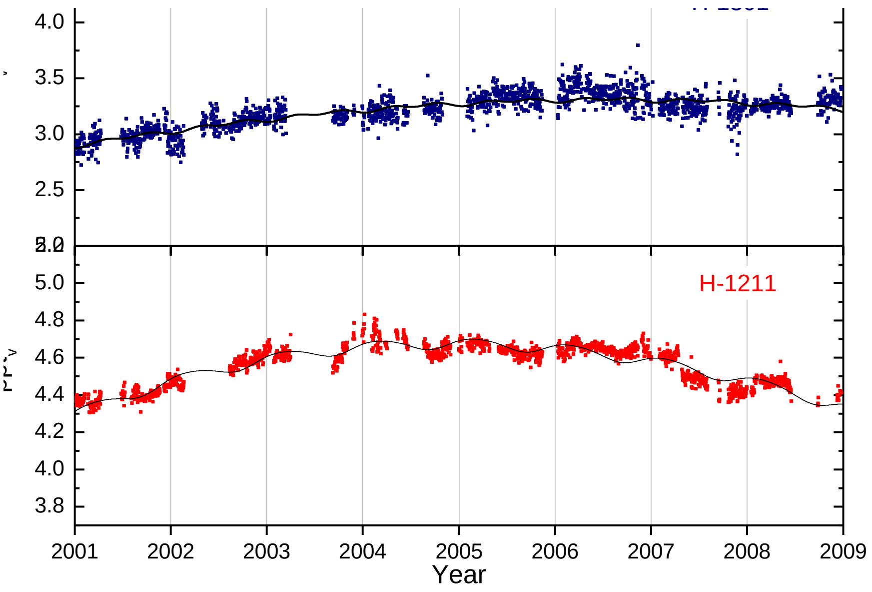

Figure 20: Daily average concentrations of the monitored halons: H-1301 (blue in the upper panel) and H-1211 (Red in the lower panel) for the period 2001-2008 at the Zeppelin observatory. The solid lines are modelled background mixing ratio.

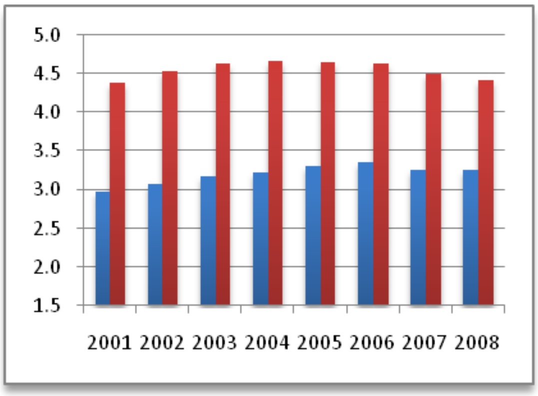

Figure 21: Development of the annual means the observed Halons at the Zeppelin Observatory for the period 2001-2008. Red: Halon-1211, Blue: H-1301.

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 2001-2008 shows a small increase for both substances in total, with a very small reduction in the rates indicating that the trend is expected to be lower 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 which is 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 2001-2008

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 sources of all these substances are solvents. The daily averaged concentrations are shown in Figure 22.

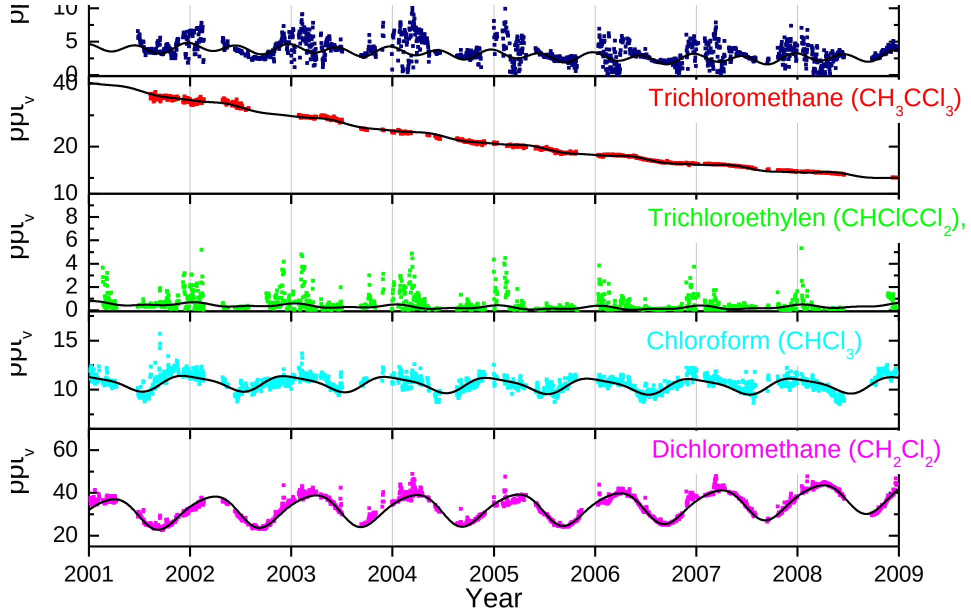

Figure 22: Daily average concentrations chlorinated hydrocarbons: From the upper panel: Perchloroethylene (dark blue) Trichloromethane (red), Trichloroethylen (green), Chloroform (light blue) and Dichloromethane (pink) for the period 2001-2008 at the Zeppelin observatory. The solid lines are the modelled background mixing ratio.

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 2001-2008. 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 3.83 ppt per year for the period 2001-2008, a total reduction of more than 70% since 2001. For Dichloromethane there is an increase of 22% since 2001.

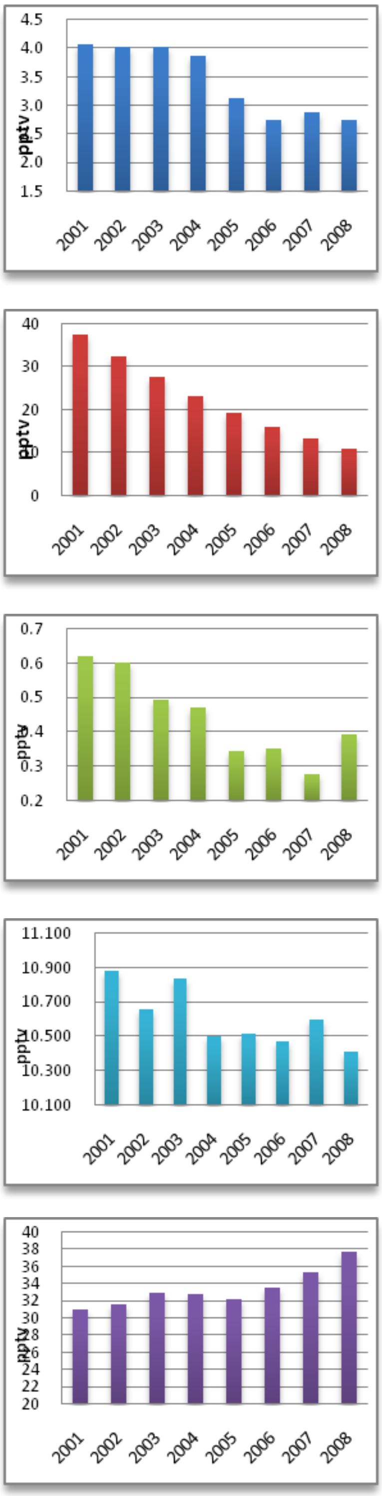

Figure 23: Development of the annual means of the chlorinated hydrocarbons. From the upper panel: Perchloroethylene (blue), Trichloromethane (red), Trichloroethylen (green), Chloroform (light blue) and Dichloromethane (violet) for the period 2001-2008.

Trichloromethane (CH_3CCl_3) 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).

3.2.6 Perfluorinated compounds

The only perfluorinated compound measured at Zeppelin is Sulphurhexacloride, SF_6. This is an extremely strong 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_2. The other perfluorinated compounds are also very powerful greenhouse gases thus NILU plan to extend the monitoring programme with Carbon Tetrafluoride (CF_4) and possibly also Hexafluoroethane (C_2F_6) from 2010, when we have new and improved instrumentation installed at Zeppelin. The current instrumentation is not well suited for measurements of SF_6 thus there are larger uncertainties in this compound than in most of the other compounds reported. The daily averaged concentration of SF_6 is presented in Figure 24. The compound is increasing with a rate of 0.2 ppt/year, and has increased by 33% since the start in 2001.Note that the variations through the year is not due to seasonal variations, rather it is instrumental adjustments.

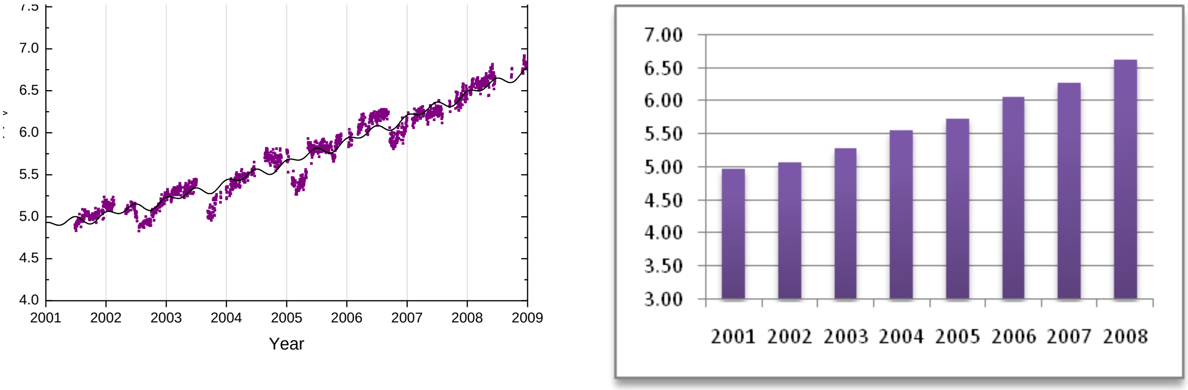

Figure 24: Daily average concentrations of SF_6 for the period 2001-2008 to the left, and the development of the annual mean concentrations in the right panel.

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.

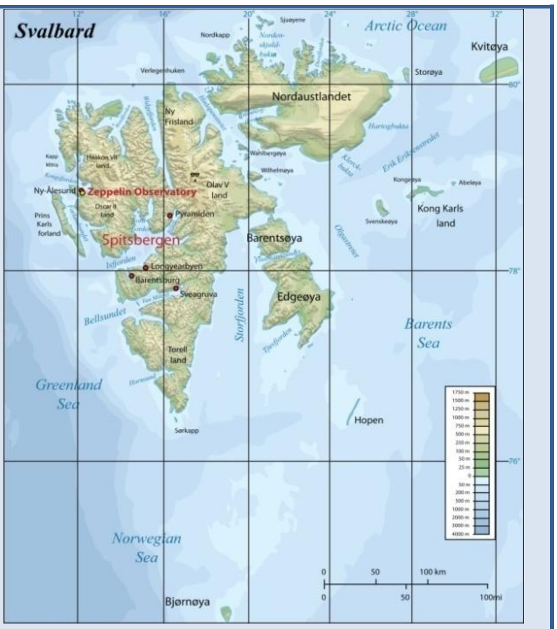

Figure 25: The monitoring station is located at the Zeppelin Mountain at Spitsbergen close to the village Ny-Ålesund.

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_2 at Zeppelin observatory

At the Zeppelin station carbon dioxide (CO_2) 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_2 monitoring project at the Zeppelin station has three goals:

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

SU has several instruments at Zeppelin station, which measure particles in the atmosphere. Aerosols 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). A total filter allows creating a bi-daily record of the chemical composition of aerosol particles.

4. Observations of the total aerosol load above Ny-Ålesund, Svalbard

In the investigations of climate change, aerosols are of vital interest, as they cause significant effects on the radiative balance of the Earth, both directly, through scattering and absorption of short-wave and long-wave radiation, and indirectly, by acting as condensation nuclei. Calculations of the effects of aerosols still have a high level of uncertainty despite the huge scientific focus during the last decades (IPCC, 2007).

Aerosols vary considerably by regions and respond quickly to changes in emissions as their lifetime is short, in the order of days-weeks. Major sources of anthropogenic aerosols are fossil fuel and biomass burning. Aerosols like sulphate, biomass burning aerosols and fossil fuel organic carbon results in negative radiative forcing (cooling), while black carbon from fossil fuel and fires has a positive forcing (warming effect). 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 Polar regions with high surface albedo due to snow and ice, aerosols can produce appreciable warming at the surface. Shindell and Faluvegi (2009) conclude that decreasing concentrations of sulphate aerosols and increasing concentrations of black carbon at mid latitudes may have substantially contributed to rapid Arctic warming during the past three decades. Interestingly, Eleftheriadis et al (2009) report decreased levels of black carbon at Svalbard in the period 1998-2007. Improving our knowledge of polar aerosols and their radiative impacts is important in order to arrive at a more realistic evaluation of changes in the Earth's radiative balance, especially when polar albedo can change because of reductions in sea ice and changes in snow cover.

To address topics related to the radiative forcing by Polar aerosols in particular, a program referred to as POLAR-AOD has been approved as a major 'cluster' project to be undertaken during the International Polar Year (IPY). The measurements of the total aerosol load in Ny-Ålesund contributed to this network and first results can be found in Tomasi et al. (2007).

4.1 Measurements of the total aerosol load above Ny-Ålesund in 2008

The Precision-Filter-Radiometer (PFR) accurately measures direct solar radiation transmitted in 4 narrow spectral bands. From these measurements, the atmospheric Aerosol Optical Depth (AOD) can be determined by a collection of algorithms. AOD is a measure of the scattering and absorption of visible light by particles in a vertical column of the atmosphere and it is proportional to the total concentration of particulates in the atmosphere.

The 2008 measurement season started at the end of February and lasted until end of September as the measurements require direct sun light. AOD results are covering the time period between March 12th and July 10th. Overcast weather conditions and instrumental alignment problems resulted in rejection of measurements after that date. Hourly averaged AOD values (at 500 nm) measured in Ny-Ålesund are presented in Figure 26. Only hours with more than 10% of valid observations are included.

The AOD observations shown in Figure 26 show increased aerosol levels during the Arctic haze period in the spring. However, there are also short episodes in the summer with slightly higher levels of AOD in June (around June 20th) and July 4th. Thin aerosol layers aloft are caused by long-range transport of aerosols into the Arctic.

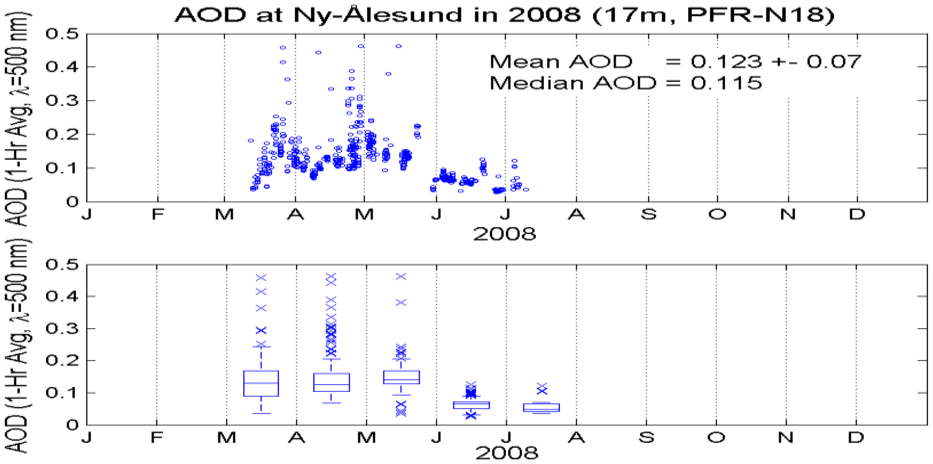

Figure 26: Hourly averaged AOD values at 500 nm, measured in Ny-Ålesund during 2008.

Table 3 gives an overview of the spring/summer and monthly mean values for AOD at 500 nm and the Ångström exponent α. α is derived for each set of measurements by linear regression through log(AOD(λ)) versus log(λ/1000nm) using all four PFR channels. The Ångström exponent, α, provides information about the size of the aerosols. Larger values of α imply a relatively high ratio of small particles.

The measurements from 2008 are revealing the expected pattern, larger AOD, tantamount to higher aerosol-load in spring than in summer, where background conditions were seen with low aerosol column concentration. The Ångström coefficients increase from spring to summer with large loading of fine aerosols seen in summer.

Table 3: Annual and monthly mean values of AOD at 500 nm together with the Ångström coefficients α in Ny-Ålesund in 2008.

Month	AOD at 500 nm Mean / Median / Std. dev.	Ångström coefficient α Mean / Median / Std. dev.	Number of hours with observations
March	0.14 / 0.13 / 0.07	1.36 / 1.44 / 0.32	143
April	0.15 / 0.12 / 0.08	1.30 / 1.29 / 0.28	246
May	0.15 / 0.14 / 0.05	1.39 / 1.44 / 0.18	191
June	0.06 / 0.06 / 0.02	1.45 / 1.64 / 0.37	202
July	0.06 / 0.05 / 0.03	1.49 / 1.43 / 0.27	23
March - July	0.12 / 0.11 / 0.07	1.37 / 1.43 / 0.30	805

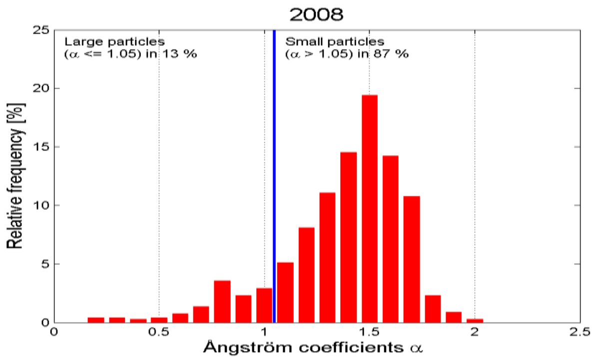

Figure 27: The relative frequency of hourly averaged Ångstrøm coefficient, α, during 2008.

In Figure 27 relative frequencies of hourly averaged Ångström exponents, α, during 2008 are displayed. The α values show a distinct peak around α = 1.5. About 87% of the α is in the range from 1.05-2, and around 13% are below 1.0 in Ny-Ålesund, the typical threshold value for larger marine aerosol types (Smirnov et al., 2003). This is comparable to 2007, but much less than in 2006 where 40% of the values were in this range (see Figure 29). The high α values imply large loading of fine aerosols typical for long-range transport.

In general aerosols transported over a wider area are small compared to primary local source aerosols as sea salt. 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 Ångström exponent. The smallest aerosols are found every year 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.

The transition from spring-time to summer has been analysed using multi-year observations of aerosols at Svalbard (Engvall et al., 2008). The authors show the transition from an accumulation-dominated (90-630 nm) to an Aitken-dominated distribution (22-90 nm) occurs over the period April through June and suggest that the aerosol microphysical properties are not only the result of transport, but of a delicate balance between incoming solar radiation, transport, and condensational sink processes. How and to what extent processes in the boundary layer and the free troposphere are inter-linked is not clear yet. In order to get better insight into this phenomenon, not only ground-based and total column measurements, but in-situ measurements covering the whole troposphere are necessary.

4.2 Measurements of the total aerosol load above Ny-Ålesund in 2002-2008

The time series of eight years is too short for trend analysis. However, we have calculated monthly mean and sun-light season averaged values to compare the years and the seasonal variations. The number of observations are shown in Table 4.

Table 4: Number of observations (hourly averages).

Month/Year	2002	2003	2004	2005	2006	2007	2008	Total
March		28	11	43	46	-	116	244
April	19	137	31	123	95	156	201	762
May	90	89	83	141	-	101	154	658
June	62	21	37	73	15	92	152	452
July	25	83	25	67	71	135	16	422
August	40	129	69	32	33	72	-	375
September	56	57	46	55	65	77	-	355
Mar-Sep	292	544	302	534	325	633	639	3270

Monthly mean AOD values are presented in Figure 28 and in Table 5.

Figure 28 presents the AOD measurements at 500 nm in Ny-Ålesund for the years 2002-2008. The AOD values are, as expected, considerable higher during the Arctic haze period for all years than during the summer months. The results show clear seasonal variations, but also some inter-annual variability. Individual episodes can have a large contribution to this observed variability. Analyses of such episodes are important to understand the effect of pollution transported into the region. Stohl and co-workers (Stohl *et al.* 2006) 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 end of July 2004. Agricultural fires in Eastern Europe resulted in elevated pollution levels in Arctic in spring 2006 (Stohl et al., 2007) and 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.

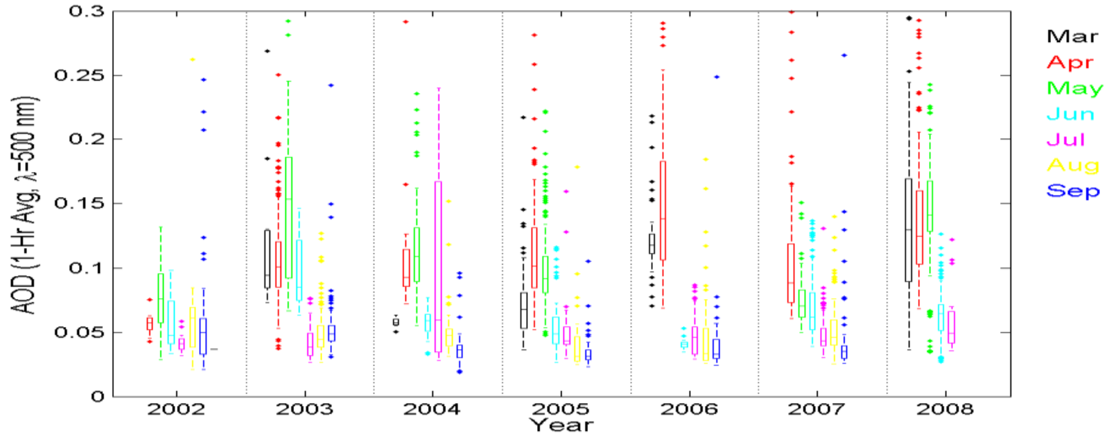

Figure 28: Monthly average aerosol optical depth (AOD at 500 nm) measured in Ny-Ålesund during the sunlight time periods in 2002 - 2008. On each box, the central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers (in terms of monthly averages, although not considered outlier in terms of pollutions events with high aerosol loads) are plotted individually.

Table 5: Monthly mean and sunlight-season average values of AOD at 500 nm measured in Ny-Ålesund between 2002 and 2008. The values given are mean, median and standard deviation.

Month/Year	2002	2003	2004	2005	2006	2007	2008	2002-2008
March		0.15/0.09/0.12	0.06/0.06/0.00	0.08/0.07/0.03	0.12/0.12/0.03		0.14/0.13/0.07	0.12/0.11/0.07
April	0.06/0.06/0.01	0.11/0.10/0.05	0.12/0.09/0.08	0.12/0.10/0.07	0.16/0.14/0.07	0.10/0.09/0.05	0.15/0.12/0.08	0.13/0.11/0.07
May	0.08/0.08/0.03	0.15/0.15/0.06	0.13/0.11/0.09	0.10/0.09/0.03		0.10/0.07/0.12	0.15/0.14/0.05	0.12/0.10/0.07
June	0.06/0.05/0.02	0.10/0.09/0.03	0.06/0.06/0.01	0.05/0.05/0.02	0.04/0.04/0.00	0.07/0.06/0.03	0.06/0.06/0.02	0.06/0.06/0.02
July	0.07/0.04/0.12	0.04/0.04/0.01	0.10/0.06/0.07	0.05/0.04/0.02	0.05/0.05/0.02	0.05/0.04/0.01	0.06/0.05/0.03	0.05/0.04/0.04
August	0.07/0.06/0.08	0.05/0.04/0.02	0.05/0.05/0.02	0.04/0.03/0.03	0.05/0.03/0.04	0.05/0.05/0.02		0.05/0.05/0.04
September	0.06/0.05/0.05	0.06/0.05/0.03	0.04/0.04/0.02	0.03/0.03/0.01	0.04/0.03/0.03	0.04/0.04/0.03		0.05/0.04/0.03
Mar – Sep	0.07/0.06/0.05	0.09/0.07/0.06	0.08/0.06/0.07	0.08/0.07/0.05	0.09/0.06/0.07	0.07/0.06/0.06	0.12/0.11/0.07	0.09/0.07/0.07

In Figure 29 relative frequencies of hourly averaged Ångström exponents, α, for the time period 2002 to 2008 are displayed. The data are given as averaged values separate for each year (2002-2008, upper panel) and each months (March-September, lower panel). The data values are displayed in Table 6. The amount of large particles varies from over 40% (in 2006) to less than 10% in 2007, although one has to be aware of that this values are not absolutely comparable due to a change of data coverage (see Table 4 for number of contribution measurements). The transition from Arctic Haze to summer can be seen in the relative frequency distribution for the individual months. The smallest aerosols are found every year during summer (11% large particles compared to 33% in March) 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. More research is needed to estimate the underlying processes (transport versus local contribution and aerosol micro-physics).

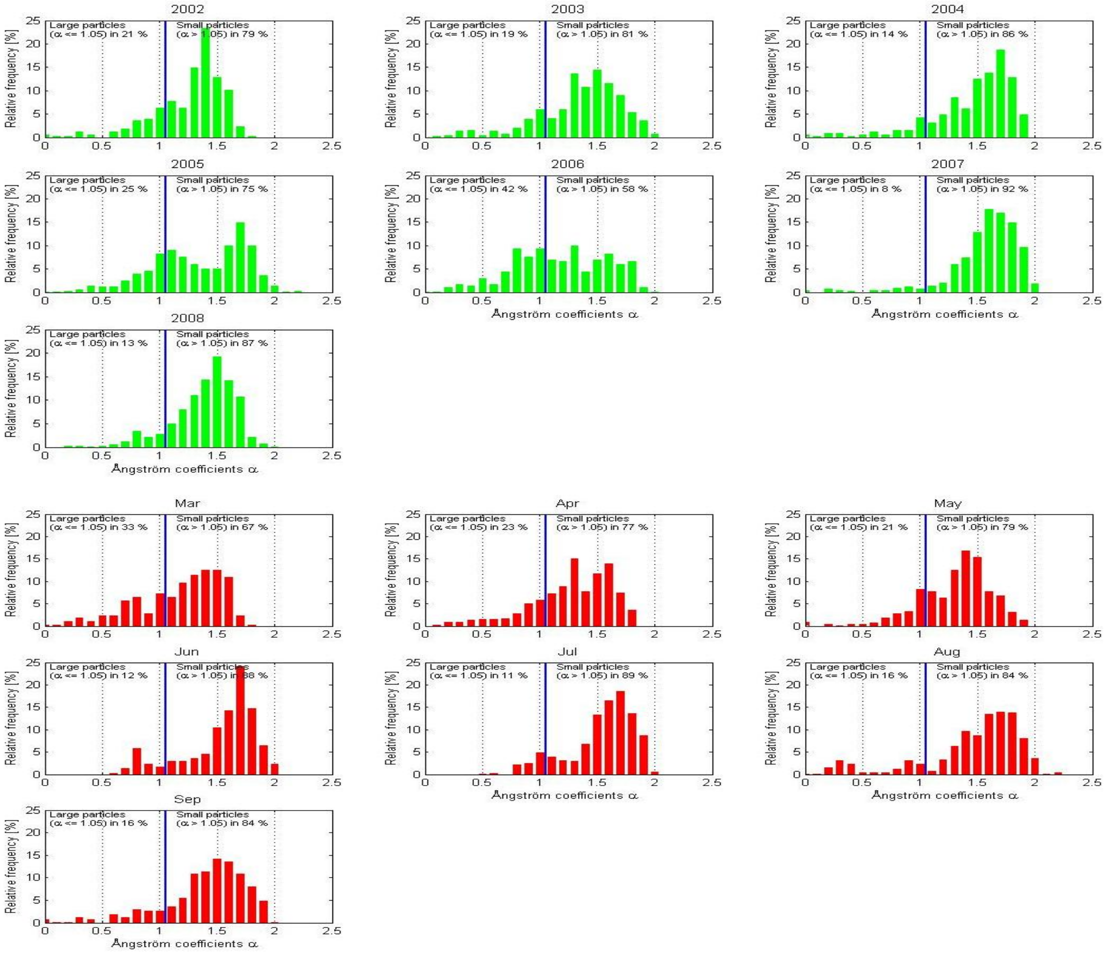

Figure 29: The relative frequency of hourly averaged Ångstrøm coefficient, α, during 2002 to 2008 (upper panel) and during March to September (lower panel).

Table 6: Monthly mean and sunlight-season average values of Ångström coefficient α measured in Ny-Ålesund in the period between 2002 and 2008. The values given are mean, median and standard deviation.

Month/Year	2002	2003	2004	2005	2006	2007	2008	2002-2008
March		0.9/1.1/0.5	1.3/1.3/0.1	1.1/1.2/0.3	0.9/0.8/0.1		1.4/1.4/0.3	1.2/1.3/0.4
April	0.9/1.0/0.1	1.3/1.3/0.3	1.2/1.3/0.3	1.4/1.6/0.4	0.9/0.9/0.3	1.4/1.5/0.4	1.3/1.3/0.3	1.3/1.3/0.4
May	1.4/1.4/0.1	1.3/1.3/0.2	1.4/1.6/0.5	1.0/1.0/0.2		1.4/1.5/0.6	1.4/1.4/0.2	1.3/1.4/0.4
June	1.2/1.3/0.3	1.5/1.5/0.1	1.7/1.7/0.2	1.6/1.7/0.3	1.7/1.7/0.2	1.7/1.8/0.2	1.5/1.6/0.4	1.5/1.6/0.3
July	1.2/1.1/0.2	1.5/1.6/0.3	1.6/1.6/0.4	1.7/1.7/0.2	1.4/1.5/0.3	1.6/1.7/0.2	1.5/1.4/0.3	1.5/1.6/0.3
August	1.3/1.4/0.4	1.4/1.5/0.5	1.5/1.6/0.3	1.4/1.6/0.7	1.3/1.5/0.6	1.7/1.8/0.3		1.5/1.6/0.5
September	1.2/1.4/0.5	1.4/1.5/0.3	1.3/1.3/0.3	1.5/1.6/0.4	1.4/1.3/0.3	1.5/1.6/0.4		1.4/1.5/0.4
Mar-Sep	1.3/1.3/0.3	1.3/1.4/0.4	1.4/1.6/0.4	1.3/1.4/0.4	1.2/1.2/0.4	1.5/1.6/0.4	1.4/1.4/0.3	1.4/1.5/0.4

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 and aerosols. We have analysed the origin of the air arriving at Zeppelin in 2008. Air mass trajectories are calculated using the FLEXTRA trajectory model (http://tarantula.nilu.no/trajectories/) and using meteorological data provided from ECMWF (European Centre for Medium Range Weather Forcasts). 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.[3] 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'.

Air from the Arctic and Atlantic sector is assumed to contain minimal influence of pollution. There are no industrial sources in these areas, and one can say that the air is 'clean'. Background values of the greenhouse gases components are defined from those 'clean air' areas with 6 out of 8 trajectories (sampling day +/- 12 hours) within the sector, as described above.

Figure 30 shows the share of polluted and clean air arriving at Zeppelin observatory for the years 2001-2008.

In 2008 there were several episodes with polluted air transported to Zeppelin but no episodes as extreme as the record one observed in 2006 (Stohl et al., 2007; Myhre et al 2007). Rather it is important to emphasise the high frequency of days with air categorised as clean arctic marine air (75%) for 2007 and 2008 (70%) compared to the previous years. This is air from the Atlantic region and north of 65 degrees from the northern parts of Scandinavia, Russia, Greenland, USA and Alaska. This means that the observations at Zeppelin were less influenced by air from central Europe in 2007 and 2008 than previous years.

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[3] 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.

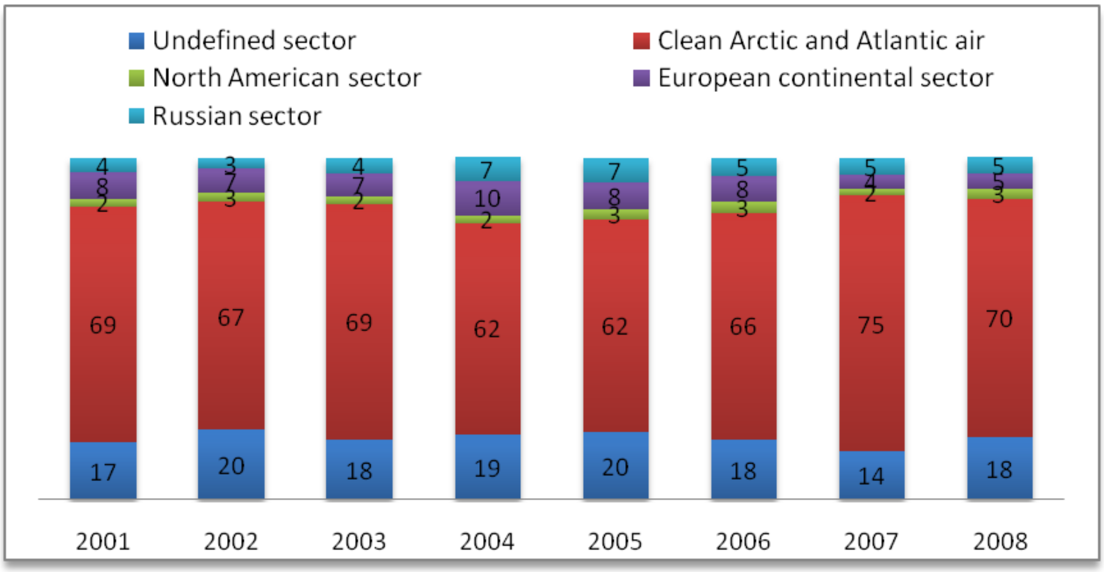

Figure 30: The percentage of polluted and clean air arriving at Zeppelin in the period 2001-2008 from the various sectors.

5.1 Regional emissions and the influence on methane levels

We have performed a more detailed analysis of the air masses for the days and periods with elevated methane levels in 2008. In Figure 31 are the methane observations for the period 2001-2008 shown together with an indication if the air masses are considered as clean Arctic and Atlantic air or polluted air.

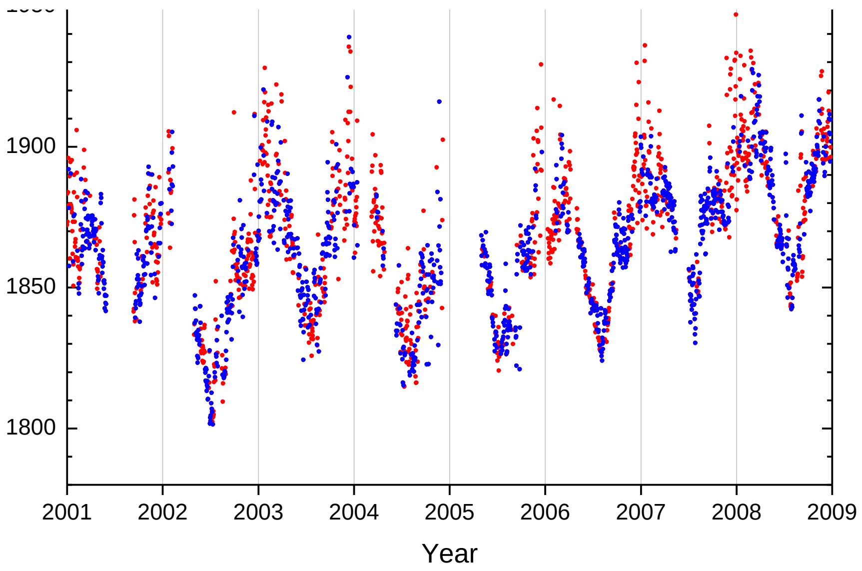

Figure 31: Observations of methane for the period 2001-2008 at the Zeppelin observatory. Blue dots: air mass origin is from a clean sector, red dots: the air mass origin is from a polluted sector.

The blue dots represent the background methane level, which means 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 and 2008 a large portion of the air masses arriving at Zeppelin originate from the Arctic and Atlantic sector. Further, the peak episodes are due to pollution transported from lower latitudes.

We have analysed a selection of the peak episodes for 2008 on methane further. In the upper panel of Figure 32 are the observations for 2008 shown, and in the lower panel are FLEXPART simulations for 16th January shown.

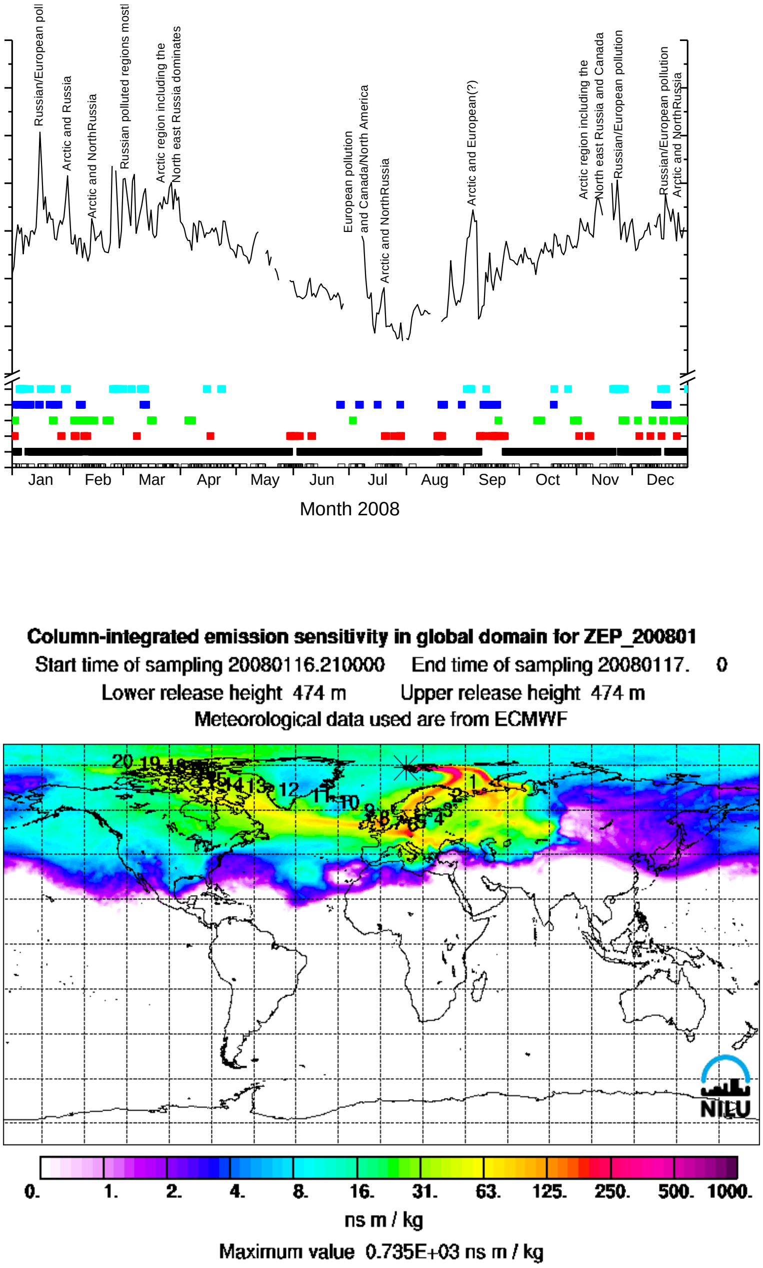

Figure 32: Upper panel: Methane observations for 2008 with an indication of source regions for the elevated episodes. Lower panel: FLEXPART simulations for 16th January.

An approximate indication of the source region of the episodes is included in Figure 32 to the left. This is based on an analysis of FLEXTRA simulations for the selected days. The coloured marks at the bottom of the Figure indicate the various sectors as described on page 44. In the lower panel are FLEXPART simulations for 16th January shown. At this day there were very high levels of CH_4, CO, and CO_2 and also elevated levels of halocarbons observed. The FLEXPART simulations show that the dominating source regions of the air influencing Zeppelin the last 21 days before these observations are the central Europe, and Northern Russia particularly the areas with oil and gas installations. This is a typical situation for long range transport of pollution from the continents industrialised regions.

6. Measuring methane from space

Trough the SatLuft project financed by The Norwegian Space Centre NILU has been given the opportunity to assess the various sources of satellite-derived CH_4. One of the main objectives has been to investigate the potential of using these data in monitoring methane over a larger geographical region in Scandinavia and Arctic, and to provide quantitative estimates of CH_4 for climate studies with a particular emphasis on the Arctic region.

In the study we used as many sources of satellite derived CH_4 data as possible and data from MIPAS and IMG (ADEOS) were to be considered. However, these data, in one case provide measurements only in the stratosphere (MIPAS) and, in the second case, for a very limited time period (IMG). Thus our efforts have been focused on data from SCIAMACHY, AIRS and IASI. These data do not provide sufficient resolution (space, time and accuracy) to be of great use for understanding the sources of CH_4, since it is generally accepted that these are confined to the layers of the atmosphere closest to the surface. Nevertheless, it has been worthwhile investigating the strengths and weaknesses of the satellite data because this may lead to improvements, or at least a better specification for the requirements of future satellite instruments.

Atmospheric CH_4 measurements from satellites are currently restricted to daytime, poor temporal and spatial resolution and estimates of column abundance only. Some infrared measurements providing night time observations have recently become available, but these also have poor temporal and spatial resolutions. There is a strong need to develop new methods and instrumentation for CH_4 measurements and deploy these in the Arctic.

6.1 Current Satellite CH_4 Measurements

There is no satellite instrument specifically dedicated to the measurement of CH_4. Rather, the instruments that are used have multiple purposes, usually with a capability of measuring a few gases well and other gases to an acceptable level of accuracy. Instruments that can measure CH_4 well generally do so in regions of the atmosphere far from the surface (e.g. MIPAS) or with very limited spatial and temporal resolution. This is unfortunate because the region of the atmosphere where CH_4 needs to be measured is close to the surface. SCIAMACHY (The Scanning Imaging Absorption spectroMeter for Atmospheric CHartography) was launched on ESA's Envisat satellite platform in 2002. The instrument has more than 8000 channels making spectral measurements from the ultraviolet (0.24 µm) up to the near infrared (2.39 µm). CH_4 is a target gas for this instrument, but note that the instrument was not specifically designed to measure CH_4.

The dry air column-averaged mole fraction (or mixing ratio), is retrieved from SCIAMACHY. The light path variation is determined by retrieving CO_2 in a different waveband, which provides a measure of the number of air molecules within the vertical column, and then normalized with a global average CO_2 mixing ratio (370 ppm is used). This can introduce errors and a bias into the determination of CH_4, since CO_2 varies around the globe, and a constant value is used.

Some retrieval products from SCIAMACHY compared with TM5 model estimates (Bergamaschi et al., 2007) are shown in Figure 33.

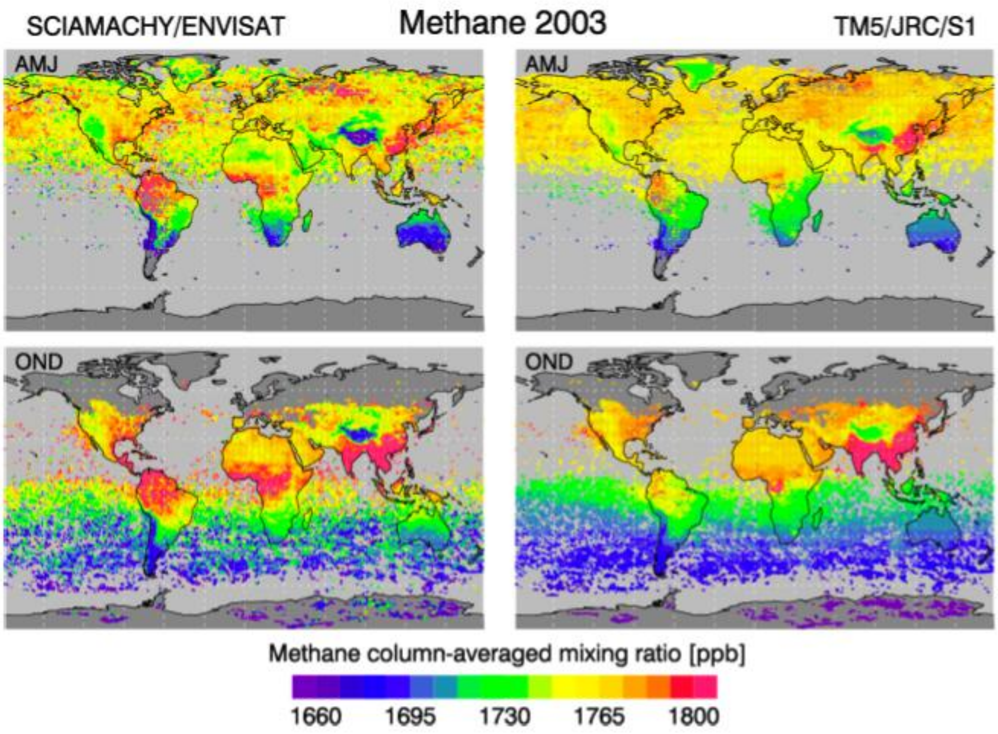

Figure 33: 3-month (seasonal) dry air column averaged XCH4 mixing ratios (ppb) determined from SCIAMACHY. Left-hand panels: SCIAMACHY measurements. Right-hand panels: TM5 model.

Some salient points can be made about these maps:

- There is continental-scale information in the distributions. For example there are noticeably large CH_4 emissions over regions of south-east Asia, presumably from rice fields.
- Low emissions occur over the Southern Oceans, Greenland and arid regions (e.g. Australia) as might be expected.
- During the autumn period in the NH, no retrievals can be made at high latitudes, due to low light levels while the reverse occurs during the SH autumn at high latitudes.
- Transport phenomenon and emission sources and sinks are difficult to detect in these large-scale, temporally averaged maps.
- The general patterns between observation and TM5 model results are very similar, suggesting that at this scale (space and time) SCIAMACHY provides reliable information.

Although not explicitly shown in these maps, most of the information in the SCIAMACHY measurements arises from a very broad layer of atmosphere extending from the surface to the top of the atmosphere (~100 hPa). SCIAMACHY has proven the ability to detect changes in monthly to seasonal amounts of CH4 at scales of 50–100 km. Comparisons with ground-based FT-IR measurements give errors of ~1.5 % or ±25 ppb. While it remains doubtful that the SCIAMACHY data are able to discern changes less than a few percent even at the largest (global) scales, detection of the annual cycle at Zeppelin (about 5%, see Figure 31) is possible.

It also seems clear that SCIAMACHY measurements are unable to detect changes in the atmospheric layers closest to the surfaces, where most of the sources are. Once the CH_4 has risen, mixed and suffered transport, SCIAMACHY provides valuable information.

6.1.1 SCIAMACHY analyses above Zeppelin

In order to make a better assessment of the SCIAMACHY CH_4 retrievals, the complete 3-year data-set was downloaded from the University of Bremen site after registering and communicating with one of the PIs. The data are global, 0.5° x 0.5 ° monthly mean column abundances with error fields. For this preliminary study, the data are plotted as time-series at several locations where ground based CH_4 measurements are available. A comparison with the ground-data is not made because it is not the purpose to investigate accuracies but rather suitability for use of the data at local scales. Because the data are so sparse, spatial means were computed and plotted together with the total time-series. The error fields were not consulted: caution is therefore urged when assessing the precision and accuracy of these data.

Time-series for SCIAMACHY data for the Ny Ålesund site (Zeppelin) at 78.9 °N, 11.88 °E are show in the Figure. Data for the whole region within the rectangular box [5–30°E, 76–84 °N] were averaged; even so only 5 months produce a meaningful value over the entire 36-month record. On this basis alone we may reject any possibility of using these data for either validation or to investigate variability in time or space. A comparison with the observations presented in Figure 3 on page 16 also clearly shows that the satellite data are too low. An example of the spatial variability around this site is shown in Figure 35.

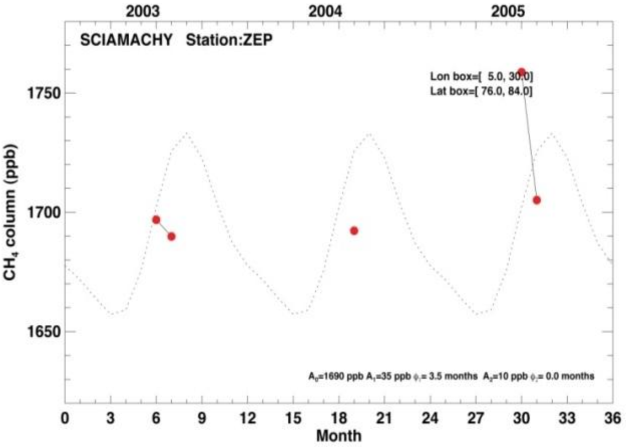

Figure 34: SCIAMACHY monthly mean averages over the spatial box indicated in the plot for January 2003 to December 2005, close to the Zeppelin station.

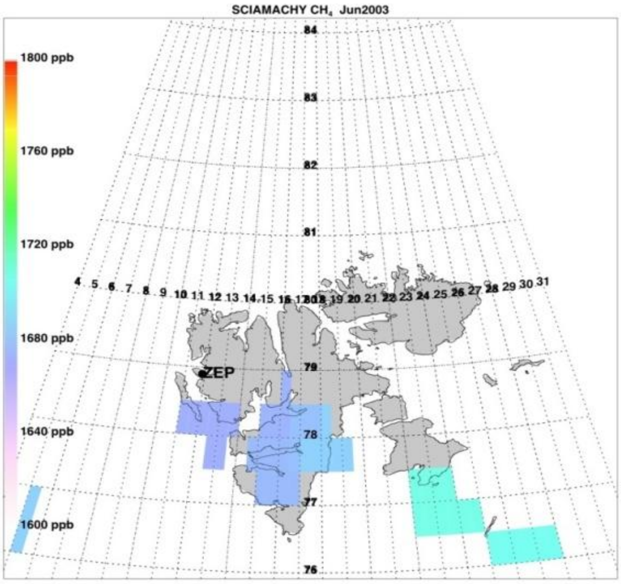

Figure 35: SCIAMACHY coverage of the Zeppelin station in June 2003

6.2 Preliminary recommendations

The preliminary recommendations based on this study for the region close to Zeppelin are that current SCIAMACHY, AIRS and IASI satellite measurements of CH_4 are not capable of providing the temporal and spatial resolution needed in order to quantify and understand near-surface variations in $CH_{4.}$ The analyses done with the measurements from the Zeppelin observatory shows clearly that the satellite data are neither suitable nor of sufficient resolution to understand processes there, or provide valuable information for validation. A similar conclusion may be made for the AIRS, IASI and GOSAT data; however a more detailed analysis needs to be done.

It seems that a major driver in changes in the growth or decline of atmospheric CH_4 in the atmosphere is due to changes in the sinks–principally the [OH], and the sources–wetlands, rice cultivation, biomass burning, coal mining, oil and gas exploration, fossil fuel use, industrial processes, ruminants and others, and potentially temperature changes in the polar latitudes inducing emissions from the permafrost. All of these sources are close to the earth's surface. Thus it seems sensible to try to measure these emissions near the surface. The analyses presented here suggest that current and planned satellite-based instruments will not be capable of capturing these variations. Since there is great uncertainty and also potentially large emissions possible from thawing of the Arctic permafrost it would seem obvious to prioritise future satellite-based measurements of CH_4 in this direction.

7. Greenhouse Gas Monitoring Networks

7.1 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 air-parcels with their location and time of origin, so it is possible to identify the various sources that contribute to the concentrations measured at the network sites. The results will contribute to the assessment of compliance with the Kyoto and Montreal protocols, and they will be utilised also to define criteria for future monitoring of halocarbons in Europe.

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

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

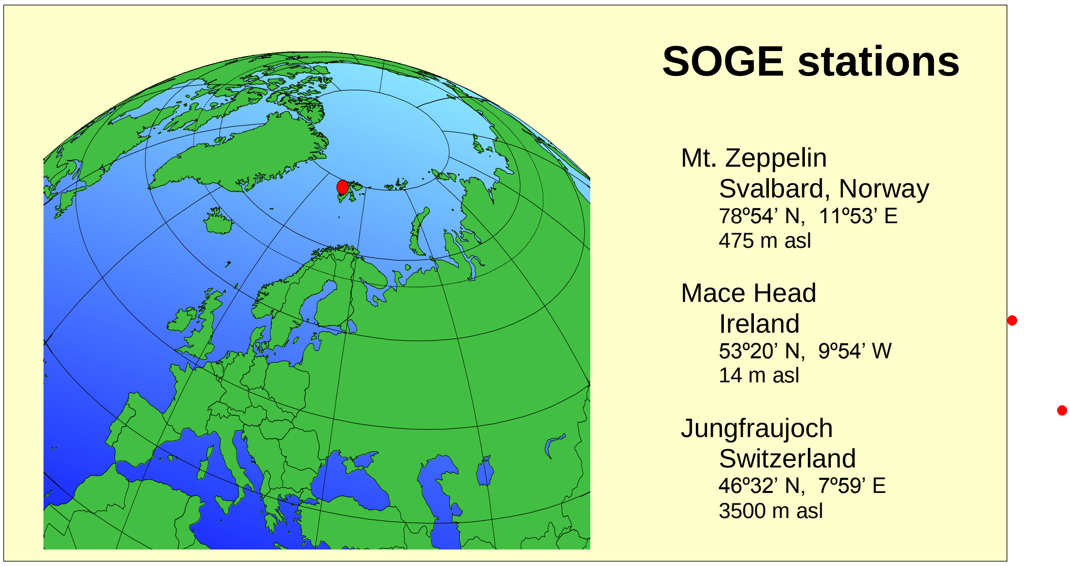

Figure 36: The SOGE climate gas monitoring stations.

7.2 AGAGE

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

The scientific objectives of AGAGE are 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 behaviour of the biogenic/ anthropogenic gases N_2O, CH_4, CO, H_2, CH_3Cl, CH_3Br, $CHBr_3$, CH_3I, CH_2Cl_2, CCl_2CCl_2 and $CHCl_3$ over the globe.
- To optimally determine the average concentrations and trends of OH radicals in the troposphere by determining the rate of destruction of atmospheric CH_3CCl_3 and other hydrohalocarbons from continuous measurements of their concentrations together with industrial estimates of their emissions.
- To optimally determine, using CH_4 and N_2O data (and theoretical estimates of their rates of destruction), the global magnitude and distribution by semi-hemisphere or region of the surface sources of CH_4 and N_2O.
- To provide an accurate data base on the rates of accumulation of trace gases over the globe which cab be used to test the synoptic-, regional- and global-scale circulation predicted by three dimensional models and/or to determine characteristics of the sources of these gases near the stations.

The AGAGE coastal measurement sites around the world are 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.

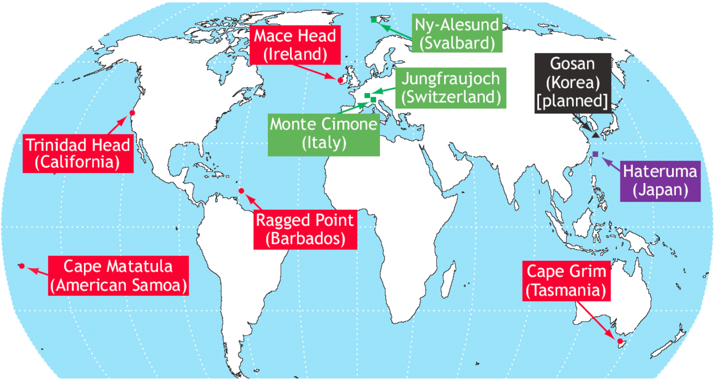

Figure 37: The AGAGE network of monitoring stations.

8. References

Bergamaschi, P., Frankenberg, C., Meirink, J.F., Krol, M., Dentener, F., Wagner, T., Platt, U., Kaplan, J. O., Körner, S., Heimann, M., Dlugokencky, E.J. and Goede, A. (2007) Satellite chartography of atmospheric methane from SCIAMACHY onboard ENVISAT 2. Evaluation based on inverse model simulations. *J. Geophys. Res*., *112*, D02304, doi:10.1029/2006JD007268.

Engvall, A.-C., Krejci, R., Ström, J., Treffeisen, R., Scheele, R., Hermansen, O. and Paatero, J. (2008) Changes in aerosol properties during spring-summer period in the Arctic troposphere. *Atmos. Chem. Phys*., *8*, 445–462.

Eleftheriadis, K., Vratolis, S. and Nyeki, S. (2009) Aerosol black carbon in the European Arctic: Measurements at Zeppelin station, Ny-Ålesund, Svalbard from 1998–2007. *Geophys. Res., Lett., 36,* L02809, doi:10.1029/2008GL035741.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. and Van Dorland, R. (2007) Changes in atmospheric constituents and in radiative forcing. In: *Climate Change 2007: The physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change*. Ed. by Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller. Cambridge, Cambridge University Press.

IPCC (2007) Summary for Policymakers. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Ed.d by Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller. Cambridge, United Kingdom and New York, Cambridge University Press.

Keppler, F., Hamilton, J.G., Bra, M. and Röckmann, T. (2006) Methane emissions from terrestrial plants under aerobic conditions. *Nature, 439*, 187-191.

Myhre, C.L., Toledano, C., Myhre, G., Stebel, K., Yttri, K.E., Aaltonen, V., Johnsrud, M., Frioud, M., Cachorro, V., de Frutos, A., Lihavainen, H., Campbell, J.R., Chaikovsky, A.P., Shiobara, M., Welton, E.J. and Tørseth, K. (2007) Regional aerosol optical properties and radiative impact of the extreme smoke event in the European Arctic in spring 2006. *Atmos. Chem. Phys., 7,* 5899-5915.

Rigby, M., Prinn, R.G., Fraser, P.J., Simmonds, P.G., Langenfelds, R.L., Huang, J., Cunnold, D.M., Steele, L.P., Krummel, P.B., Weiss, R.F., O'Doherty, S., Salameh, P.K., Wang, H.J., Harth, C.M., Mühle, J. and Porter, L.W. (2008) Renewed growth of atmospheric methane. *Geophys. Res. Lett.*, 35, L22805, doi:10.1029/2008GL036037.

Shindell, D. and Faluvegi, G. (2009) Climate response to regional radiative forcing during the twentieth century. *Nature Geosci., 2,* 294-300.

Simmonds, P.G., Manning, A.J., Cunnold, D.M., Fraser, P.J., McCulloch, A., O'Doherty, S., Krummel, P.B., Wang, R.H.J., Porter, L.W., Derwent, R.G., Greally, B., Salameh, P., Miller, B.R., Prinn, R.G. and Weiss, R.F. (2006) Observations of dichloromethane, trichloroethene and tetrachloroethene from the AGAGE stations at Cape Grim, Tasmania, and Mace Head, Ireland. *J. Geophys. Res*., *111*, D18304, doi:10.1029/2006JD007082.

Stohl, A., Berg, T., Burkhart, J.F., Fjǽraa, A.M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W.W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K. and Yttri, K.E. (2007) Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring 2006. *Atmos. Chem. Phys.*, *7*, 511-534.

Tomasi, C., Vitale, V., Lupi, A., Di Carmine, C., Campanelli, M., Herber, A., Treffeisen, R., Stone, R.S., Andrews, E., Sharma, S., Radionov, V., von Hoyningen-Huene, W., Stebel, K., Hansen, G.H., Myhre, C.L., Wehrli, C., Aaltonen, V., Lihavainen, H., Virkkula, A., Hillamo, R., Ström, J., Toledano, C., Cachorro, V.E., Ortiz, P., de Frutos, A.M., Blindheim, S., Frioud, M., Gausa, M., Zielinski, T., Petelski, T. and Yamanouchi, T. (2007) Aerosols in polar regions: A historical overview based on optical depth and in situ observations. *J. Geophys. Res.*, *112*, D16205, doi:10.1029/2007JD008432.

WMO (2007) Scientific assessment of ozone depletion: 2006. Geneva, World Meteorological Organization (Global Ozone Research and Monitoring Project – Report No. 50).

WMO (2009) Greenhouse Gas Bulletin. The state of greenhouse gases in the atmosphere using global observations through 2008. Geneve (Bulletin No. 5, 23 November 2009). http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/ghg-bulletin2008_en.pdf.

Appendix A

Description of instruments, methods and trend analysis

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 X 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	CH_4	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	CO	GC-MgO/UV	1 h	Every 2 hours, working std. calibrated vs. GAW std.	Data coverage 2007: 95%
Carbondioxide	CO_2		1 h		CO2 measurements performed by ITM Stockholm University (SU)
CFC-11	$CFCl_3$	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.
CFC-12	CF_2Cl_2				
CFC-113	$CF_2ClCFCl_2$				
CFC-115	CF_3CF_2Cl				
HFC-125	CHF_2CF_3				
HFC-134a	CH_2FCF_3				
HFC-152a	CH_3CHF_2				
HCFC-22	CHF_2Cl				
HCFC-141b	CH_3CFCl_2				
HCFC-142b	CH_3CF_2Cl				
H-1301	CF_3Br				
H-1211	CF_2ClBr				
Methyl Chloride	CH_3Cl				
Methyl Bromide	CH_3Br				
Methylendichloride	CH_2Cl_2				
Chloroform	$CHCl_3$				
Methylchloroform	CH_3CCl_3				
TriChloroethylene	$CHClCCl_2$				
Perchloroethylene	CCl_2CCl_2				
Sulphurhexafluoride	SF_6				
Ozone	O_3		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_2, SO_4^{2-}, (NO_3^- + HNO_3) and (NH_4^+ + NH_3), main compounds in precipitation, mercury, persistent organic pollutants (HCB, HCH, PCB, DDT, PAH etc.), as well as tropospheric and stratospheric ozone.

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 26th October to 16th February, leading to short observational seasons. However during the summer it is possible to measure day and night if the weather conditions are satisfactory. The instrument measures direct solar radiation in four narrow spectral bands 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_2 and aerosol measurements performed by ITM Stockholm University (SU*)*

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

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

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

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

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

Model studies: calculation of trends

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

$$f(t) = a + b\left(\frac{N}{12}\right) \cdot P_1\left(\frac{t}{N} - 1\right) + \frac{1}{3} \cdot d\left(\frac{N}{12}\right)^2 \cdot P_2\left(\frac{t}{N} - 1\right) + c_1 \cdot \cos(2\pi t) + s_1 \sin(2\pi t) + c_2 \cos(4\pi t) + s_2 \sin(4\pi t)$$

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 inter-annual cycles in mole fraction. N is the mid-point of the period of investigation. P_i 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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Tittel - norsk og engelsk

Klimagassovervåking ved Zeppelinobservatoriet – Årsrapport 2008

Greenhouse monitoring at the Zeppelin station – Annual report 2008

Sammendrag – summary

Rapporten presenterer aktiviteter og måleresultater fra klimagassovervåkingen ved Zeppelinobservatoriet på Svalbard for årene 2001-2008.

Overvåkingsprogramet utføres av Norsk institutt for luftforskning (NILU) og er finansiert av Statens forurensningstilsyn (SFT) (nå Klima- og forurensningsdirektoratet (Klif)) og Norsk institutt for luftforskning (NILU).

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 2001-2008.

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

4 emneord Drivhusgasser, partikler, Arktis, halokarboner	4 subject words Greenhouse gases, aerosols, Arctic, halocarbons

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Om Statlig program for forurensningsovervåking

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. Klima- og forurensningsdirektoratet er ansvarlig for gjennomføringen av overvåkingsprogrammet.

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