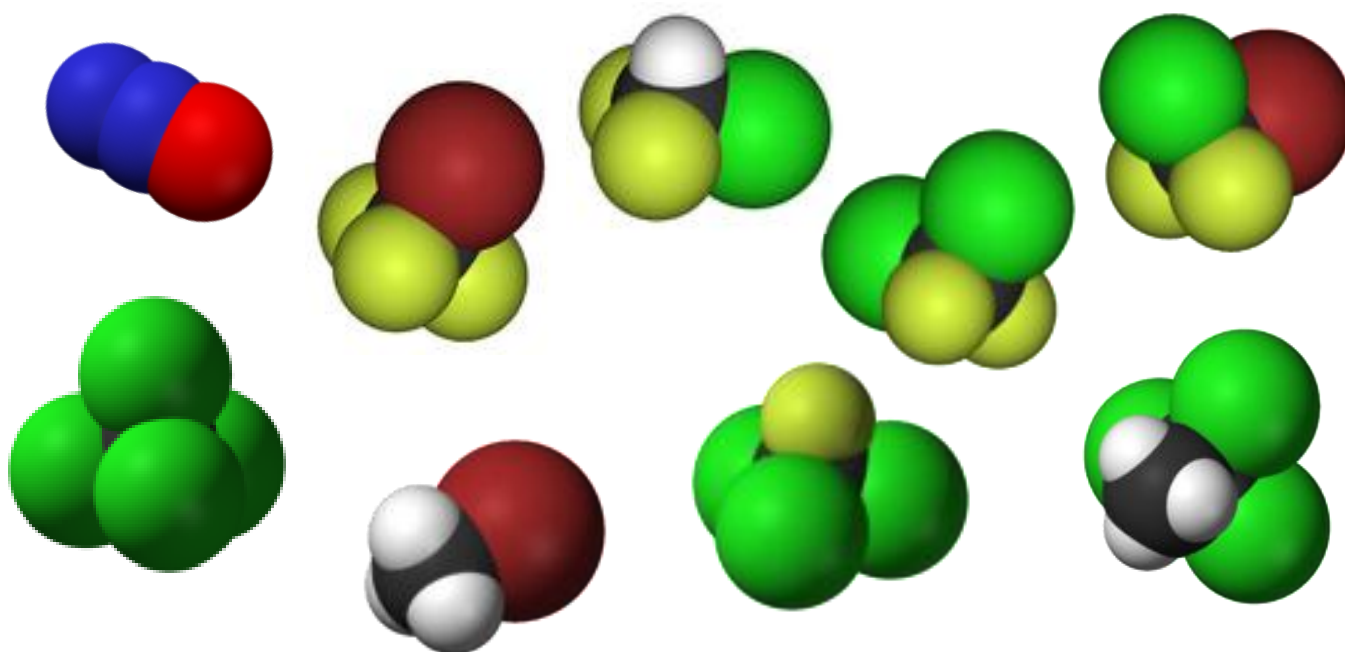


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Literature review on ODS (Ozone Depleting Substances) measurement methods and data

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Abstract

Stratospheric ozone absorbs most of the sun's harmful UV radiation. The increased use of human-produced gases such as chlorofluorocarbons (CFCs) has led to a magnified springtime depletion of the protective ozone layer at both Earth's poles, especially over Antarctica, a phenomenon well known as the ozone hole. The Montreal protocol [1] deals with substances that deplete the ozone layer (ODS) and how to reduce them (Montreal protocol, 1987 and amendments/adjustments). It covers substances with a high ozone depleting potential, CFCs and the 1st generation of CFC replacements (HCFCs). The success of the implementation of the Montreal protocol and amendments has to be demonstrated by the parties (including EU and its Member States [2]), and supported by high quality atmospheric measurements of relevant compounds. Several atmospheric data-sets are available from open-access international data bases, including 7 stations across Europe: (1) Zeppelin, Ny-Ålesund, Norway, (2) Summit, Greenland, Denmark, (3) Mace Head, Ireland, (4) Tacolneston, UK, (5) Jungfrauoch, Switzerland, (6) Monte Cimone, Italy, and (7) Lampedusa (LMP), Italy, but data quality may in some cases be unknown or questionable. High-quality long-term ambient air data are mainly coming from the AGAGE Network (<http://agage.mit.edu/> [3]) and NOAA (National Oceanic and Atmospheric Administration). Ref. [3] comprising also European stations from e.g. (I) Ireland (first Agrigole (1978-1983), then Mace Head (from 1987 to present), (II) Switzerland (Jungfrauoch), from 2000 to present, (III) Norway (Ny Ålesund), from 2000 to present, and (IV) Italy (Monte Cimone) from 2002 to present. The trends in ODS concentrations measured in-situ at ground level in Europe are consistent and, similar to the trends observed in the rest of the world (see ref. [4] containing in-situ ground level measurements, flask sampling and satellite observations), especially the downwards trend of CFCs, indicating the success of the Montreal Protocol, in limiting the atmospheric abundances of ODSs [4]. The UNEP/WMO Scientific Assessment of Ozone Depletion from 2014 states [4]: "The success of the Montreal Protocol in limiting the atmospheric abundances of ODSs is now well documented". This is confirmed by the AGAGE measurement network [3]: "International compliance with the Montreal Protocol is so far resulting in CFC and chlorocarbons abundances comparable to the target level so the Protocol is working". In contrast, it is of concern that the concentrations of HCFCs and N₂O, where the latter one being currently the single most important gas that depletes stratospheric ozone (see e.g. ref. Ravishankara et al., 2009 [15], and discussions in this report), are still increasing.

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Executive summary

Stratospheric ozone absorbs most of the sun's harmful UV radiation. The increased use of human-produced gases such as chlorofluorocarbons (CFCs) has led to a magnified springtime depletion of the protective ozone layer at both Earth's poles, especially over Antarctica, a phenomenon well known as the ozone hole. The Montreal protocol [1] deals with substances that deplete the ozone layer (ODS) and how to reduce them (*Montreal protocol, 1987 and amendments/adjustments in 1990 (London), 1991 (Nairobi), 1992 (Copenhagen), 1993 (Bangkok), 1995 (Vienna), 1997 (Montreal), 1999 (Beijing), 2007 (Montreal)*). It covers substances with a high ozone depleting potential, CFCs and the 1st generation of CFC replacements (HCFCs). The success of the implementation of the Montreal protocol and amendments has to be demonstrated by the parties (including EU and its Member States [2]), and supported by high quality atmospheric measurements of relevant compounds.

Several atmospheric data-sets are available from open-access international data bases, including 7 stations across Europe: (1) Zeppelin, Ny-Ålesund, Norway, (2) Summit, Greenland, Denmark, (3) Mace Head, Ireland, (4) Tacolneston, UK, (5) Jungfrauoch, Switzerland, (6) Monte Cimone, Italy, and (7) Lampedusa (LMP), Italy, but data quality may in some cases be unknown or questionable. High-quality long-term ambient air data are mainly coming from the AGAGE Network (<http://agage.mit.edu/> [3]) and NOAA (National Oceanic and Atmospheric Administration). Ref. [3] comprising also European stations from e.g. (I) Ireland (first Agrigole (1978-1983), then Mace Head (from 1987 to present), (II) Switzerland (Jungfrauoch), from 2000 to present, (III) Norway (Ny Ålesund), from 2000 to present, and (IV) Italy (Monte Cimone) from 2002 to present.

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Introduction I: Implementation of the Montreal Protocol

The Montreal Protocol [1] on substances that deplete the ozone layer was designed to reduce the production and consumption of ozone depleting substances (ODS) in order to reduce their abundance in the atmosphere, and thereby protect the ozone layer (ODS substances: e.g. chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and chlorinated solvents). The original Montreal Protocol was agreed in 1987 and entered into force two years later. The Montreal Protocol includes a unique adjustment provision that enables the Parties to the Protocol to respond quickly to new scientific information and agree to accelerate the reductions in emission of chemicals already covered by the Protocol as appropriate. Since its initial adoption, the Montreal Protocol has been adjusted several times. Adjustments and reductions in production and consumption of the controlled substances listed in the Annexes of the Protocol have been carried out several times between 1990 and 2007.

The European Community is a Party to the Montreal Protocol, since the Protocol addresses a transboundary environmental problem with global impact. Furthermore, regulating intra-Community and external trade in ODS and products, cannot be sufficiently achieved by the Member States acting individually and can therefore be better achieved at Community level [2]. Already by 2010, the EU had significantly reduced its consumption of the main ozone-depleting substances, 10 years ahead of its obligation under the Montreal Protocol (see e.g. http://ec.europa.eu/clima/policies/ozone/index_en.htm).

EU regulation 1005/2009 ([2]) on substances that deplete the ozone layer implements the Montreal Protocol as adjusted in 2007, but is more ambitious and stricter than the Montreal Protocol itself, e.g. through addressing future challenges, such as e.g. biocidal products (e.g. methyl bromide). The regulation lays down rules on the production, import, export, placing on the market, use, recovery, recycling, reclamation and destruction of substances that deplete the ozone layer, on the reporting of information related to those substances and on the import, export, marketing and use of products and equipment containing or relying on those substances. Atmospheric monitoring of ODS is not considered in the regulation [2], but is seen as an important tool to monitor the implementation of the Montreal Protocol.

Introduction II: Observations of ODS

The most abundant long-lived, chlorine and bromine containing gases regulated by the Montreal Protocol [1] are monitored in the Earth's atmosphere by both in-situ measurements and remote sensing.

It is important to monitor ODS for various reasons: To understand fundamental atmospheric processes and properties (abundance, lifetime and variability of ODS), to understand the human influence on ODSs abundances (quantification of human contributions and their changes, as well as natural influences), and to provide policy-relevant information (success of the implementation of the Montreal protocol and other protocols, and also to quantify the contributions of ODSs to radiative forcing). Continued measurements allow us to monitor progress of abatement strategies and identify any unexpected developments.

ODS are usually monitored by a combination of gas chromatographs with electron capture (ECD) or mass spectroscopy (MS) detectors. Instrumentation can be employed in a monitoring station, or flask sampling with subsequent centralised analysis is also carried out (see e.g. (<http://agage.mit.edu/> [3]). Furthermore, measurements are performed from various “mobile sampling platforms”, such as aircrafts, balloons, towers or ships. Remote sensing of CFCs has been reported (see e.g. Coheur et al., 2003 [5]; Hoffmann et al., 2008 [6]; Brown et al., 2011 [7]; Kellmann et al., 2012 [8]; Minschwaner et al., 2013 [9]), for example with the MIPAS instrument on the ENVISAT satellite, which was measuring mid infrared limb radiance spectra and could be used to retrieve a.o. vertical profiles of CFC-11 and CFC-12. Satellite borne spectroscopic instruments give less accurate measurements than ground based instruments, but provide a “comprehensive” spatial coverage.

More information on the three techniques and data achieved (monitoring stations, flask sampling and satellite) can also be found in ref. [4].

Measurement methods for ODS

Recommended methods for *in situ* measurements of ODS

The ongoing, surface-based observations provide a direct measure of the total number of chlorine and bromine atoms in the lower atmosphere, or troposphere. Because the lower atmosphere is quite well-mixed for these long-lived compounds, ground-level observations also provide an accurate estimate of the composition of air entering the stratosphere.

Most long-term accurate observations of ODS have been performed in the frame of the series of networks ALE, GAGE, and AGAGE, supported by multinational institutions and organisations. The instrumentation and calibration techniques evolved from ALE to GAGE to AGAGE (<http://agage.mit.edu/> [3]): With the inauguration of each new phase, measurement frequency and the number of analyzed species increased.

Using gas chromatography (GC) with an electron-capture detector (ECD), the Atmospheric Lifetime Experiment (ALE) began operation in July 1978 (until about 1986). It measured five species: CCl₃F (CFC-11), CCl₂F₂ (CFC-12), CH₃CCl₃, CCl₄, and N₂O four times daily.

This gas chromatographic experiment was succeeded in the 1981-1985 time frame by the Global Atmospheric Gases Experiment (GAGE), which measured 3 additional gases, namely CCl₂FCClF₂ (CFC-113), methane (CH₄), chloroform (CHCl₃) by using a flame ionization detector (FID), as well as the ALE suite of gases. The frequency of measurement was also increased to 12 times per day during the GAGE period (1981-1996).

A third phase, the Advanced Global Gases Experiment (AGAGE) began over the 1993-1996 period. AGAGE, which continues to the present, has two instrumental components:

- a) First a highly improved gas chromatograph multidetector (GC-MD) system (with ECD, FID, and mercuric oxide reduction detector (MRD)). It can measure 10 compounds, 36 times per day.
- b) Second, an automated gas chromatograph-mass spectrometer with an adsorption-desorption system (ADS GC-MS) at two of AGAGE stations: Mace Head, Ireland (started in October 1994), and Cape Grim, Tasmania (started in January 1998). This system can measure a wide range of hydrochlorofluorocarbons, hydrofluorocarbons (HCFC-141b, HCFC-142b, HFC-134a etc.), methyl halides (CH₃Cl, CH₃Br, CH₃I) and the halons (e.g. H-1211, H-1301).

A newly developed “state of the art”, the so-called “Medusa GC-MS instrument [3]” has been deployed (from November 2003 to June 2006) at all “five” AGAGE stations [3] and at the Scripps Institution of Oceanography (SIO) calibration laboratory. These new Medusa instruments extend the number of species measured by original ADS instruments up to 40 species (see Table 1). As a result of these improvements, the original ADS GC-MS instruments at Mace Head and Cape Grim were retired in December 2004.

Today (year 2015), it is recommended by ref. [3] to use the “Medusa GC-MS instrument” for measurements of ODS.

Methods for *satellite-borne* measurements of ODS

The composition of the Earth’s atmosphere has been measured from space for several decades. Two kinds of spectroscopic techniques have generally been implemented to measure ODS from satellites: one is based on the observation of the Sun’s spectrum attenuated by the atmosphere at sunrise and sunset (solar occultation measurements, see e.g. Bramstedt et al., 2012 [10]), the other on the observation of the sun light scattered by the Earth’s atmosphere (limb emission measurements, see e.g. Bauer et al., 2012 [11]). Space-borne measurements provide a wide coverage of the atmosphere (latitude, longitude, altitude) as a function of time. In particular, measurements are routinely made in the stratosphere, where ozone depletion takes place. However, uncertainties are larger compared to *in situ* measurements although spatial and temporal averaging of satellite data improves the measurement precision (Brown et al., 2011 [7]). Yet, significant biases can remain, e.g. due to spectroscopic errors in the retrievals (Brown et al., 2011 [7]).

Measurement stations and networks for ODS in Europe

In Europe, within the AGAGE network (<http://agage.mit.edu/> [3]) ODS data are provided from Mace Head (IRL), Jungfrauoch (CH), Ny-Ålesund (N), and the collaboration station at Monte Cimone (I), which all are global stations within the frame of the global atmospheric watch program (GAW) of the World Meteorological organization (Fig. 1).

The AGAGE network, and its predecessors (ALE, and GAGE) have been measuring the composition of the global atmosphere continuously since 1978. The AGAGE network is distinguished by its capability to measure over the globe at high frequency almost all of the important gases species in the Montreal Protocol (e.g. CFCs and HCFCs). AGAGE is part of the powerful global observing system that is measuring halocarbons, including bromocarbons, in the Earth's atmosphere. The original ALE/GAGE/AGAGE stations (Mace Head, Trinidad Head, Ragged Point, Cape Matalula, and Cape Grim) are located at coastal sites around the world chosen to provide representative measurements of trace gases whose lifetimes are long compared to global atmospheric circulation times. Four “new” stations, two in Europe (Ny-Ålesund, Jungfrauoch) and two in East Asia (Shangdianzi and Gosan) have joined the AGAGE network in recent years using the same instrument and calibration scales.

AGAGE also collaborates with stations at Hateruma Island operated by the Japanese National Institute for Environmental Studies, and Monte Cimone managed by University of Urbino, Italy.

ODS data are also provided from Summit, Greenland (DK), a regional station within GAW (Fig. 1).

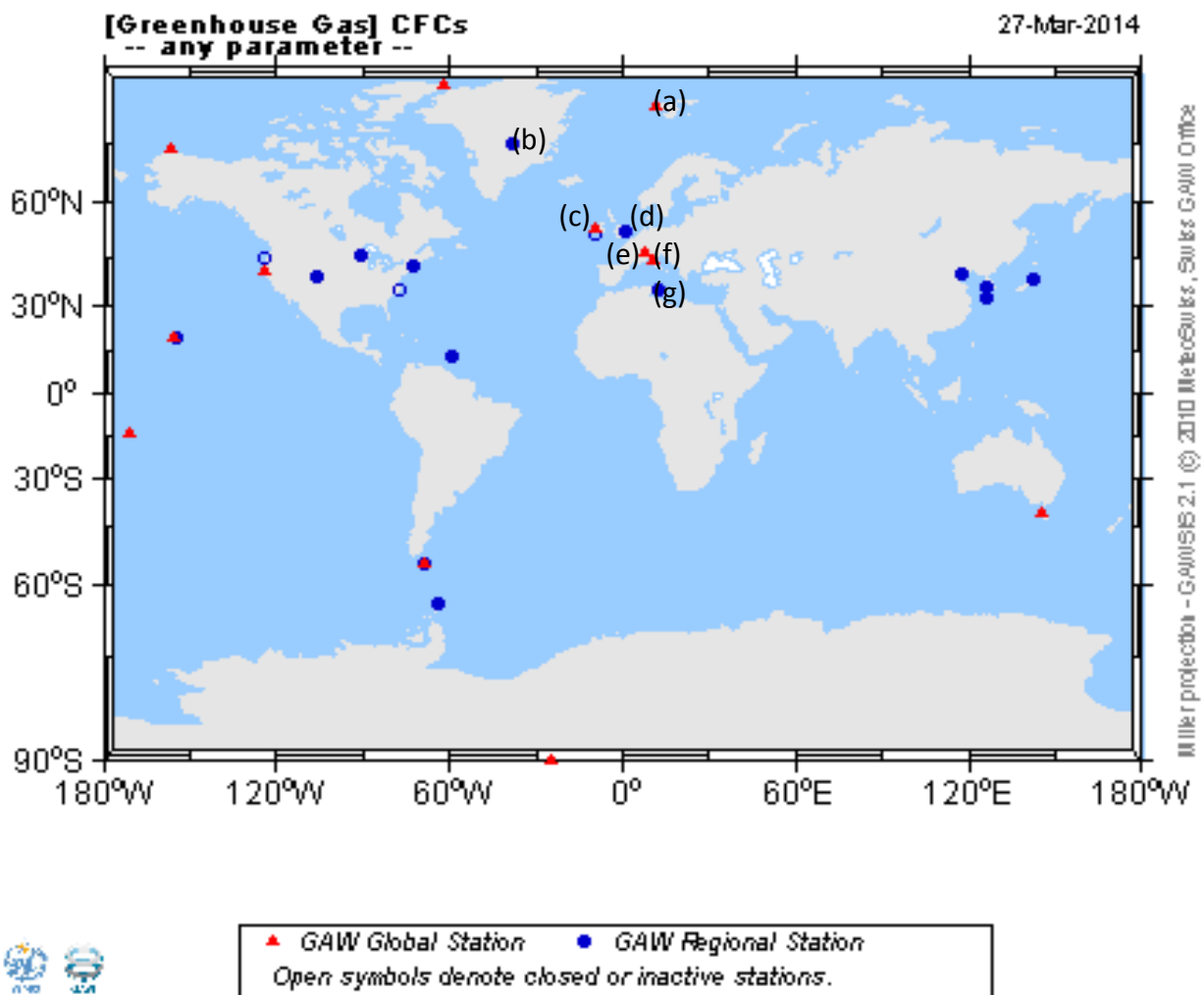


Fig. 1: The map including also the main European ODS measuring stations:

- a) Zeppelin (ZEP), Ny-Ålesund, Svalbard, Norway.
- b) Summit (SUM), Greenland, Denmark.
- c) Mace Head (MHD), Ireland.
- d) Tacolneston (TAC), UK.
- e) Jungfraujoch (JFJ), Switzerland.
- f) Monte Cimone (CMN), Italy.
- g) Lampedusa (LMP), Italy.

Source: GAW/SIS, <http://gaw.empa.ch/gawsis/>

Ground-level *in situ* measurements of ODS in Europe

The most important gaseous species currently leading to stratospheric ozone depletion are nitrous oxide, CFC-12, CFC-11, methyl bromide, methyl chloride, carbon tetrachloride, methyl chloroform, CFC-113, Halon-1211, Halon-1301, and HCFC-22, which all have an Equivalent Effective Stratospheric Chlorine (EESC) concentration larger than 10 ppt (Newman et al., 2007 [12]; Daniel et al., 2010 [13]): EESC provides an estimate of the total effective amount of halogens (chlorine and bromine) in the stratosphere. It is calculated from emission of CFCs/HCFCs and related halogenated compounds into the troposphere (lower atmosphere) and their efficiency in contributing to stratospheric ozone depletion (ozone depletion potential, ODP), and by making assumptions on transport times into the upper atmosphere (stratosphere). This parameter is used to quantify man-made ozone depletion and its changes with time. As a consequence of the Montreal Protocol and its amendments phasing out ozone-depleting substances (ODS), the EESC reached maximum in the late 1990s and is now slowly decreasing.

Some of these species have been monitored in Europe since 1987, when the Montreal protocol was agreed by the Parties. Current data series (obtained with more reliable advanced techniques) started from around 1994, which are available from open sources ([AGAGE](#) and WMO World data Centre for Greenhouse Gases, [WDCGG](#)), and flask samples from NOAA (<http://www.esrl.noaa.gov/gmd/>). See Table 1 for information about what compounds were measured. The location of the European stations are shown on a world map in Figure 1.

Table 1: Ozone depleting substance ground-level data available from stations located in Europe. Red crosses indicate that only “old data” are available (no “new data” e.g. 2013/2014/etc. are available). Blue crosses indicate that measurements are performed with the AGAGE-recommended method “MEDUSA” [3]. Black crosses indicate data available with other methods than “MEDUSA”, e.g. the flask samples from stations SUM/MHD which was obtained by NOAA: <http://www.esrl.noaa.gov/gmd/> [18].

Species	Formula	Zeppelin	Summit	Mace Head	Tacolneston	Jungfrauoch	Monte Cimone	Lampedusa
		ZEP	SUM	MHD	TAC	JFJ	CMN	LMP
Nitrous Oxide	N ₂ O	X	X	X	X	X	X	X
CFC-11	CCl ₃ F		X	X		X	X	X
CFC-12	CCl ₂ F ₂		X	X		X	X	X
CFC-113	C ₂ F ₃ Cl ₃	X	X	X	X	X		X
CFC-114	C ₂ F ₄ Cl ₂	X		X		X	X	
CFC-115	C ₂ F ₅ Cl	X		X	X	X	X	
Methyl Bromide	CH ₃ Br	X	X	X	X	X	X	X
Methyl Chloride	CH ₃ Cl	X	X	X	X	X	X	X
Carbon Tetrachloride	CCl ₄		X	X		X	X	X
Methyl Chloroform	CH ₃ CCl ₃	X	X	X	X	X	X	X
Halon-1211	CF ₂ ClBr	X	X	X	X	X	X	X
Halon-1301	CF ₃ Br	X		X	X	X	X	X
HCFC-22	CHF ₂ Cl	X		X	X	X	X	X
HCFC-141b	C ₂ H ₃ FCl ₂	X	X	X	X	X	X	X
HCFC-142b	C ₂ H ₃ F ₂ Cl	X	X	X	X	X	X	X

Nitrous oxide (N₂O)

Although N₂O is not covered by the Montreal Protocol, it leads to stratospheric ozone depleting nitrogen oxides (NO_x) and free radical reservoirs (e.g. HNO₃) in the stratosphere (Crutzen, 1970 [14]). Recent works (e.g. Ravishankara et al., 2009 [15]) indicate that for the current ozone depletion potential-weighted emissions, N₂O is actually the largest of all ozone depleting substances, and that “*a complete phase-out of anthropogenic N₂O emissions would have a larger impact on stratospheric ozone recovery than a combined phase-out of all anthropogenic chlorine- and bromine-containing ODSs*” (Daniel et al., 2010 [13]).

However, although not all stations use the AGAGE scales for calibration, all measurements clearly show a steady increase of N₂O concentrations in Europe (Fig. 2) and worldwide.

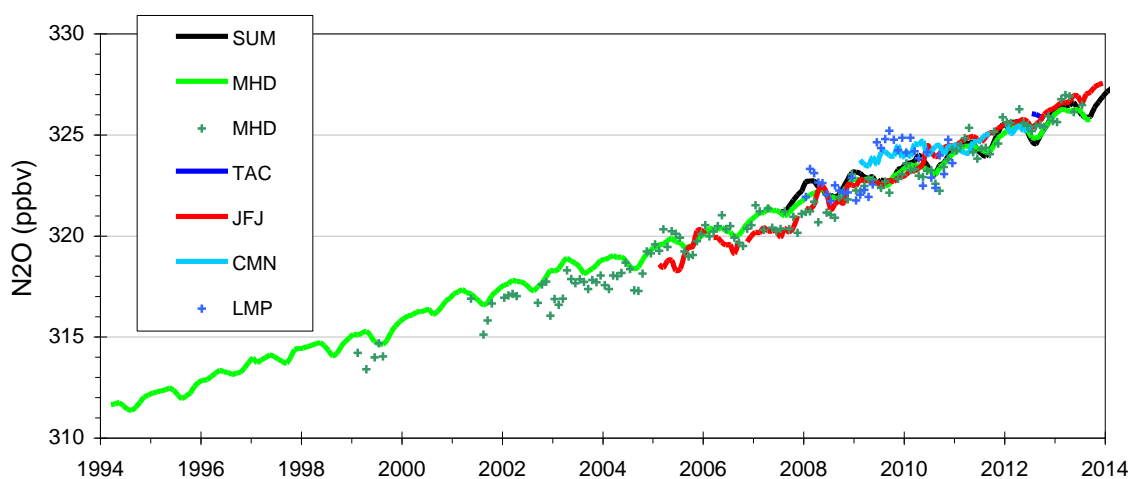


Fig. 2: Nitrous oxide concentrations (monthly averages) measured in-situ at ground level at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

Chlorofluorocarbons

CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂) are currently monitored at 4 sites in Europe. The consistency among the data obtained at these sites is sufficient to detect a constant decreasing trend over the past few years of about -0.9 and -0.5 % yr⁻¹ for CFC-11 and CFC-12, respectively (see Fig. 3).

CFC-113 (C₂F₃Cl₃) data from 3 additional European sites are available. Despite the 2 ppt offset between SUM and the other stations (mainly AGAGE partners and associates), a constant decreasing trend close to -1 % yr⁻¹ can be observed.

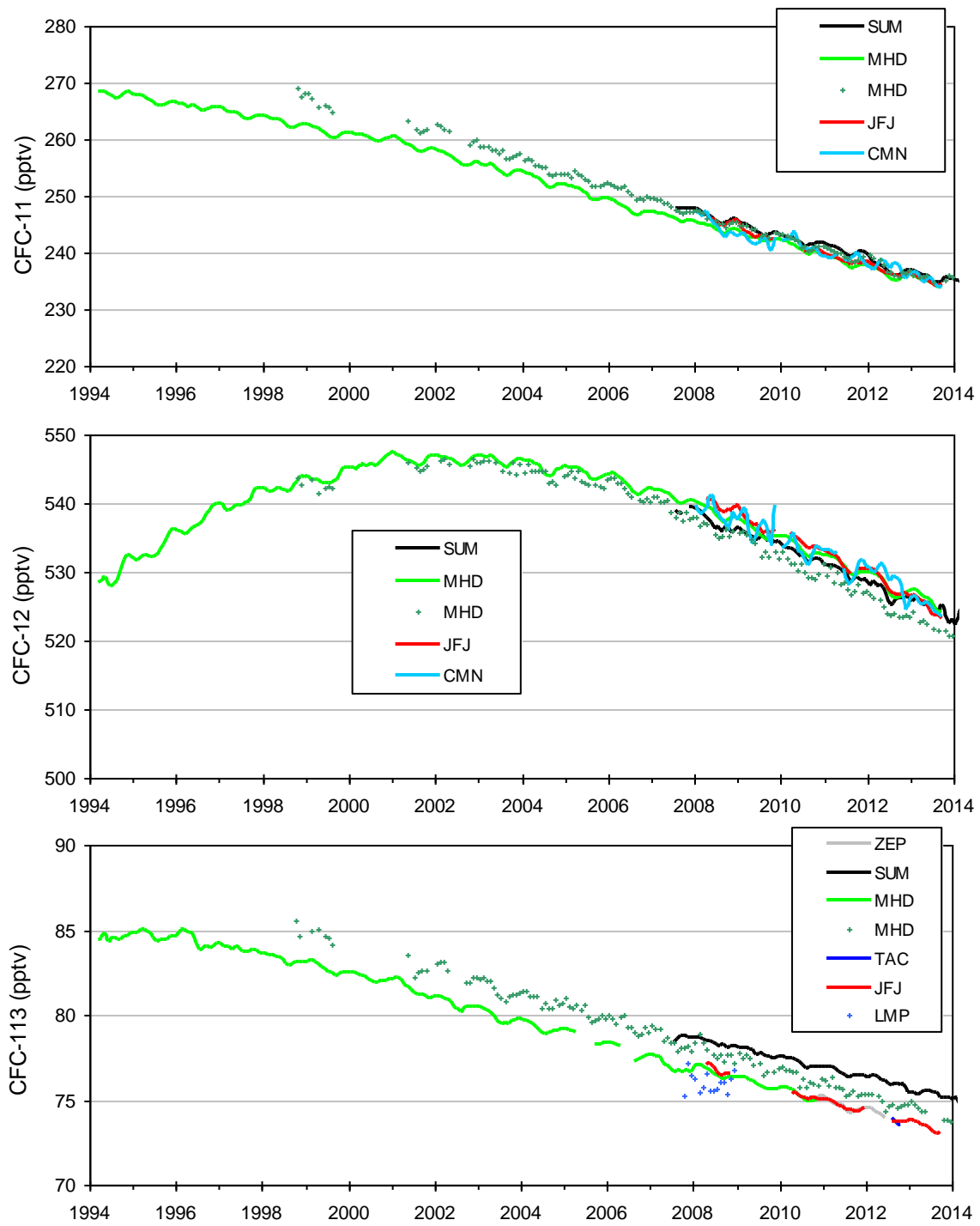


Fig. 3: *In situ* ground-level measurements of CFCs at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

Methyl bromide and methyl chloride

Methyl bromide (CH_3Br) has both natural and anthropogenic sources. In 2012, anthropogenic sources accounted for about 20 % of the CH_3Br emissions (WMO-UNEP report, 2014 [4]). Although the measurements performed at MHD and CMN lead to somewhat different data compared to ZEP, SUM, TAC and JFJ, a clear decreasing trend of about $-2\% \text{ yr}^{-1}$ over the last decade can be observed (see Fig. 4).

Methyl chloride is mostly natural with a minor (about 1 %) anthropogenic emission source. Data from the various stations are consistent and do not indicate any trend in methyl chloride concentrations over the last decade.

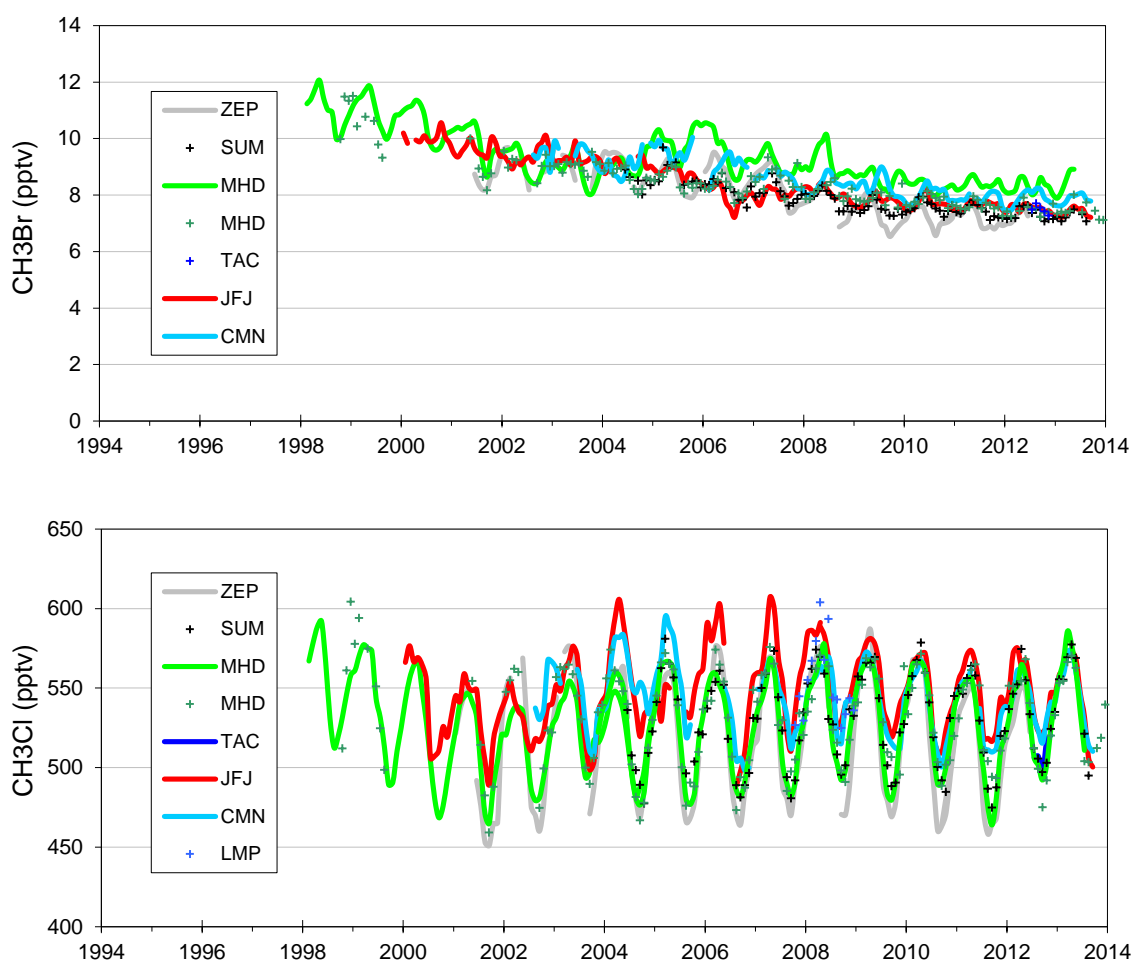


Fig. 4: *In situ* ground-level measurements of methyl bromide (top) and methyl chloride (bottom) at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

Carbon tetrachloride (CCl₄)

Despite the 2 ppt offset between the data obtained at SUM compared to the AGAGE and collaborative measurement stations, all data sets show a constant decreasing trend of about $-1\% \text{ yr}^{-1}$ over the observation period (see Fig. 5). However, CCl₄ is not decreasing as fast as expected, perhaps due to unknown or unreported anthropogenic sources (WMO-UNEP report, 2014 [4]).

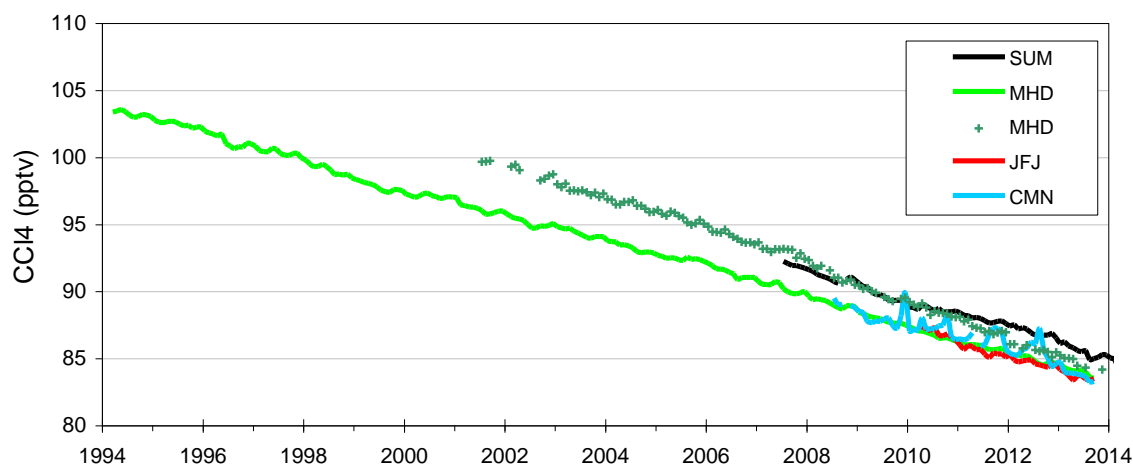


Fig. 5: *In situ* ground-level measurements of CCl₄ at various stations across Europe.

Methyl chloroform (CH₃CCl₃)

Twenty years ago, CH₃CCl₃ was one of the major stratospheric ozone depleting substances ozone killers. Measurements performed at MHD (not shown) indicate that CH₃CCl₃ concentrations peaked in the early 1990's, and started to decrease from mid-1992 onward. All measurements performed in Europe confirm a still on-going exponential decrease of about $-16\% \text{ yr}^{-1}$ (Fig. 6).

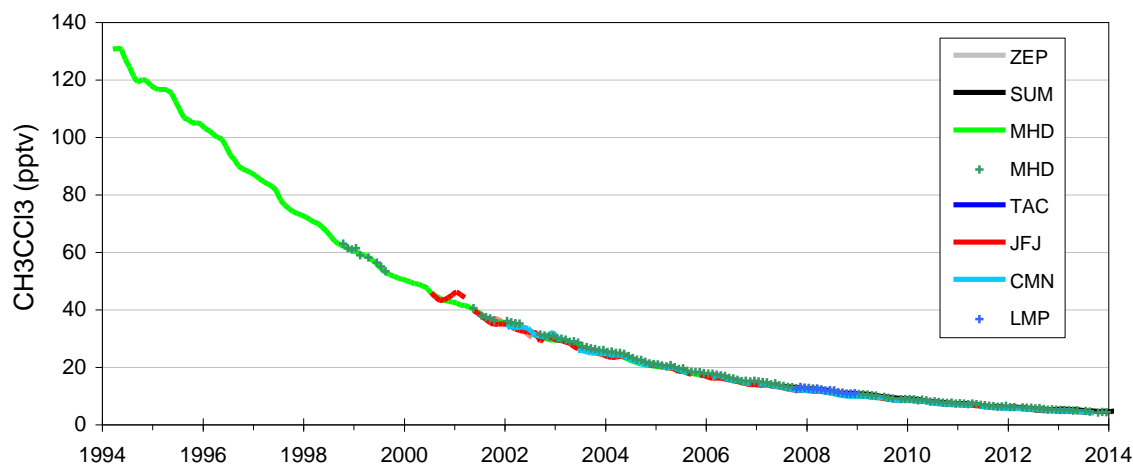


Fig. 6: *In situ* ground-level measurements of methyl chloroform at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

Halons

Halon-1211 (CBrClF₂) maximum concentrations were observed in 2004 – 2006. Over the last few years, a steady decreasing trend of about -1 % yr⁻¹ is observed at all stations.

Halon-1301 (CBrF₃) concentrations have not decreased since the late 1990's. Over the past few years, a slight increasing trend of + 0.7 % yr⁻¹ can be observed at all stations (see Fig. 7).

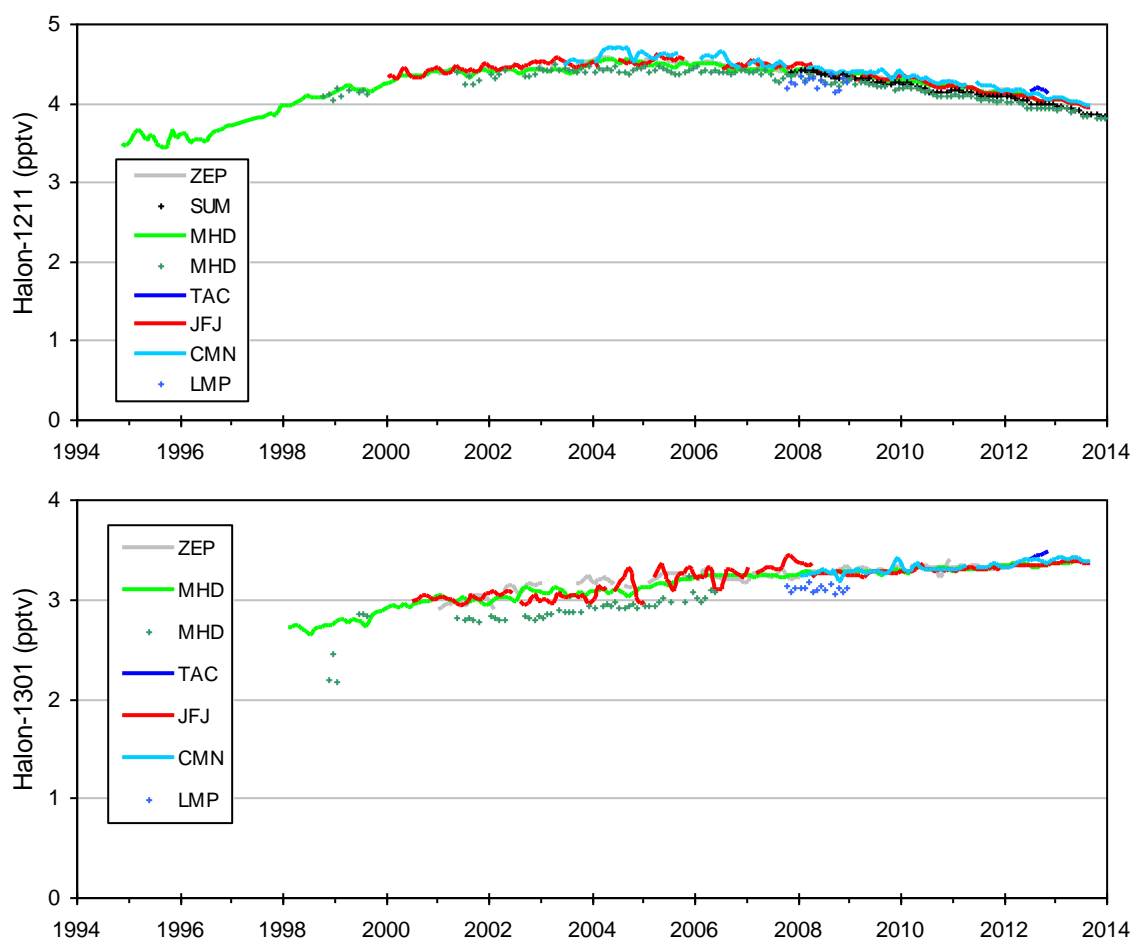


Fig. 7: *In situ* ground-level measurements of halon-1211 and halon-1301 at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

HCFCs

HCFC-22 (CHClF_2) is the only HCFC with an EESC > 10 ppt. This is also the only chlorinated species with high ozone depletion potential which shows a steep increasing trend of about $+3.5\% \text{ yr}^{-1}$ (Fig .8).

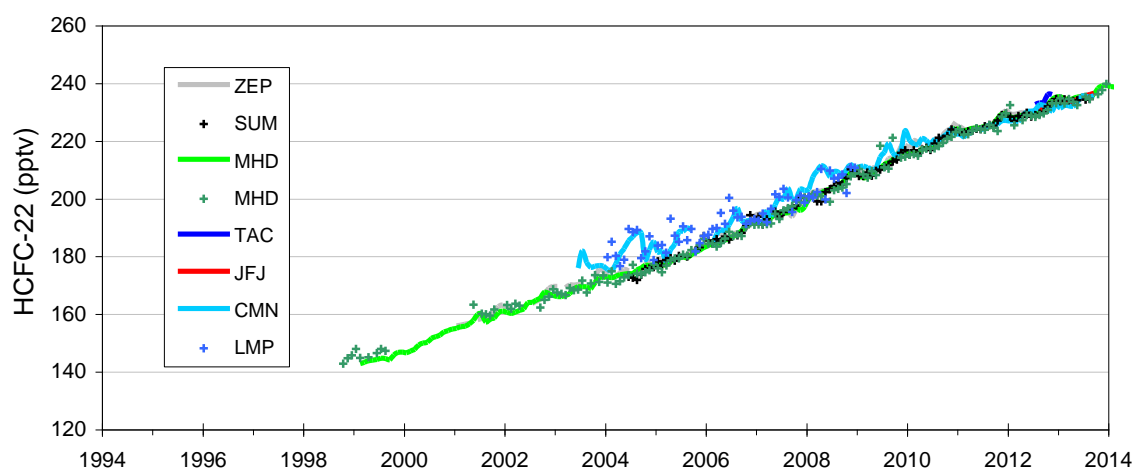


Fig. 8: *In situ* ground-level measurements of HCFC-22 at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling).

Satellite measurements of ODSs

Long-term trends derived from satellite-borne measurements have recently been obtained for various ozone depleting substances, among which nitrous oxide, CFC-11, CFC-12, CFC-113, methyl chloride, carbon tetrachloride, and HCFC-22. They can well differ from the trends measured at ground-level, depending on the altitude and latitude considered. The reasons for this include atmospheric chemistry and physics (Kellmann et al., 2012 [8]). The uncertainty of the data retrieved from satellite measurements is also much larger compared to *in situ* ground level measurements. However, the examples presented below show that satellite-borne instruments offer great possibilities for monitoring ozone depleting substances.

Nitrous oxide (N₂O)

Space-borne measurements of N₂O started in the late 1970s. Solid square symbols in Fig. 9 represent annual averages from Xiong et al. (2014) [16], obtained with AIRS (the Atmospheric Infrared Sounder), a thermal infrared sounder which was launched on the EOS/Aqua satellite in May 2002. It is sensitive to N₂O in the middle to upper troposphere. The root mean square error of AIRS measurements is 8 ppb (to be compared with the WMO-GAW relative accuracy target of 0.1 ppb for *in situ* measurements). Annual average concentrations retrieved from AIRS measurements are compared with *in situ* ground level measurements performed at European stations (Fig. 9). AIRS-N₂O concentrations at 469 hPa (about 6 km above sea level) are in better agreement with *in situ* ground level data than AIRS-N₂O concentrations at 706 hPa (about 3 km asl). However, satellite-borne and ground level measurements lead to comparable long-term trends in N₂O concentrations (Table 2).

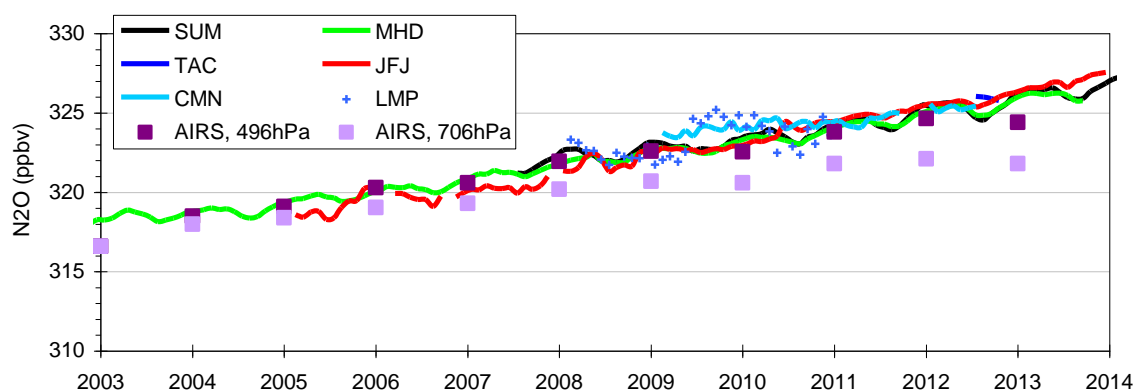


Fig. 9: Nitrous oxide concentrations (monthly averages) measured *in situ* at ground-level at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling). Purple and lavender symbols show data obtained from satellites.

Chlorofluorocarbons

CFCs have been remotely monitored from space, using instruments based on both limb sounding (e.g. the Michelson Interferometer for Passive Atmospheric Sounding, MIPAS, Kellmann et al., 2012 [8]) and solar occultation (e.g. Atmospheric Chemistry Experiment Fourier transform spectrometer ACE-FTS, Brown et al, 2011 [7]). Satellite and ground-level CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($\text{C}_2\text{F}_3\text{Cl}_3$) data are shown on Fig. 10. Despite increased seasonal variations, significant negative offsets compared to ground-level measurements and larger combined uncertainties, satellite data lead to annual trends which are consistent with those observed at European stations (Table 2).

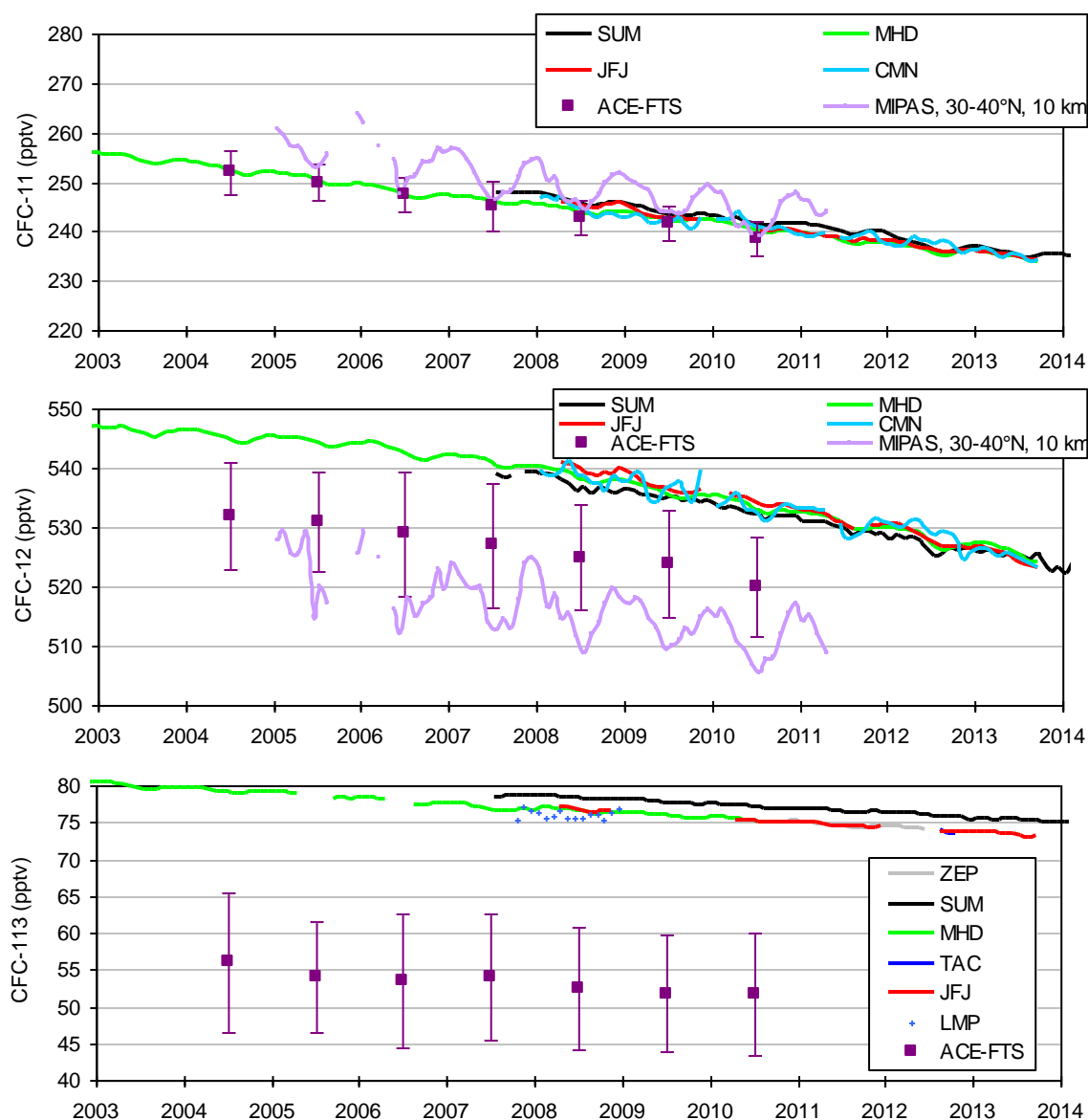


Fig. 10: Satellite-borne and in situ ground-level measurements of CFCs at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling). Purple and lavender symbols show data obtained from satellites. Squares represent annual averages between 30°N and 30°S. Error bars indicate the median absolute deviation of annual averages.

Table 2: Trends in ozone depleting substances derived from ground-level *in situ* measurements and satellite-borne instruments.

	Annual trends in ozone depleting substances (% yr ⁻¹)			
	Ground level	ACE-FTS ⁽¹⁾	MIPAS ⁽²⁾	AIRS ⁽³⁾
N ₂ O	+ 0.26 ± 0.03			+ 0.22
CFC-11	- 0.8	- 0.9 ± 0.1	- 1.07 ± 0.06	
CFC-12	- 0.4	- 0.4 ± 0.1	- 0.48 ± 0.05	
CFC-113	- 0.8	- 1.2 ± 0.1		
CH ₃ Cl	+ 0.4	+ 0.4 ± 0.2		
CCl ₄	- 1.3	- 1.2 ± 0.1		
HCFC-22	+ 4.6	+ 3.7 ± 0.1		

Ground level trends taken from Brown et al., 2011 [7], except N₂O trend which is from IPCC AR5 (2013) [17].

(1): Atmospheric Chemistry Experiment Fourier transform spectrometer on SCISAT-1 (Brown et al., 2011) [7].

(2): Michelson Interferometer for Passive Atmospheric Sounding on Envisat (Kellmann et al., 2012) [8].

(3): Atmospheric Infrared Sounder (AIRS) on EOS/Aqua (Xiong et al., 2014) [16].

Methyl chloride and carbon tetrachloride

Recent methyl chloride and carbon tetrachloride satellite data have been obtained from the ACE-FTS (Brown et al., 2011) [7]. Systematic offsets of about 15 % and 20 % compared to ground level measurements performed in Europe can be observed for CH₃Cl and CCl₄, respectively (Fig. 11). However, global trends obtained from ground-level and satellite measurements are very consistent (Table 2).

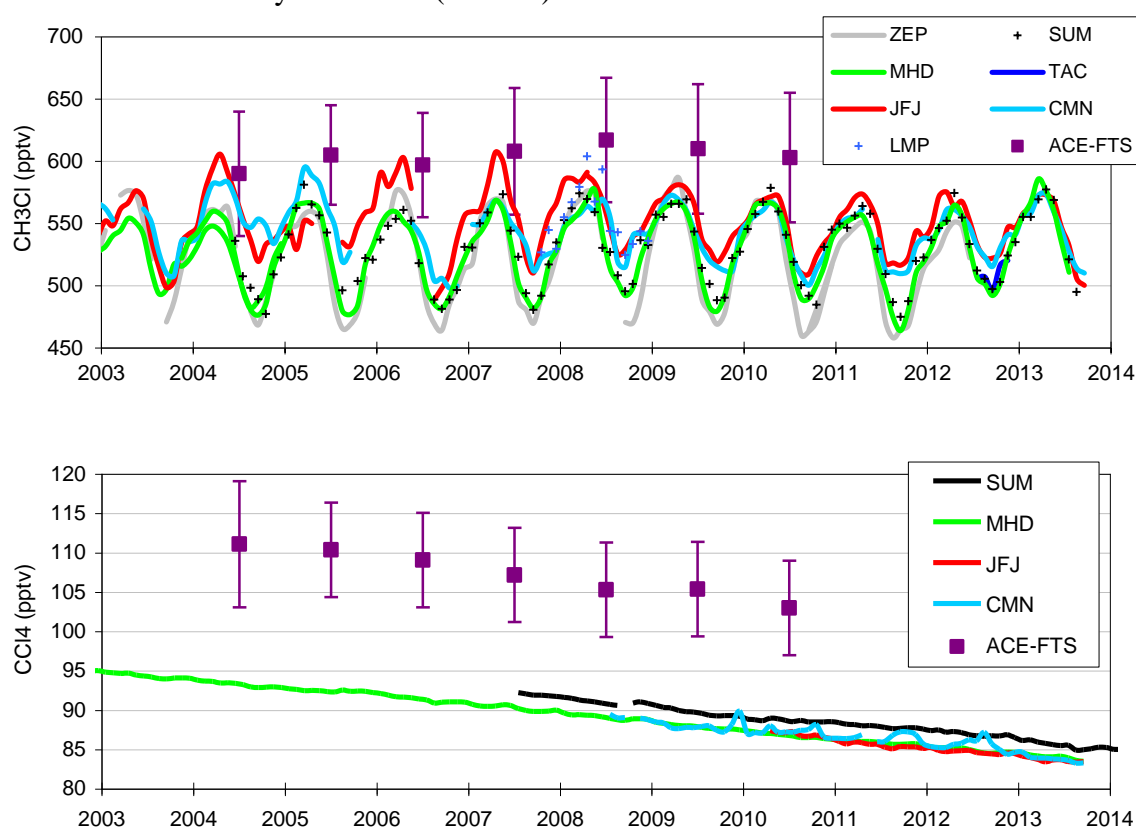


Fig. 11: Satellite-borne and *in situ* ground-level measurements of methyl chloride (top) and carbon tetrachloride (bottom) at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling). Purple squares represent annual averages obtained from satellites between 30 °N and 30 °S. Error bars indicate the median absolute deviation of annual averages.

HCFCs

HCFC-22, HCFC-141b, and HCFC-142b data have also recently been obtained from the ACE-FTS (Brown et al., 2011) [7]. The variability in HCFC-22 satellite data is particularly small, but a systematic offsets of about -10 % compared to ground level measurements performed in Europe can be observed (Fig. 12). However, the positive trends obtained from ground-level and satellite measurements are still comparable (Table 2).

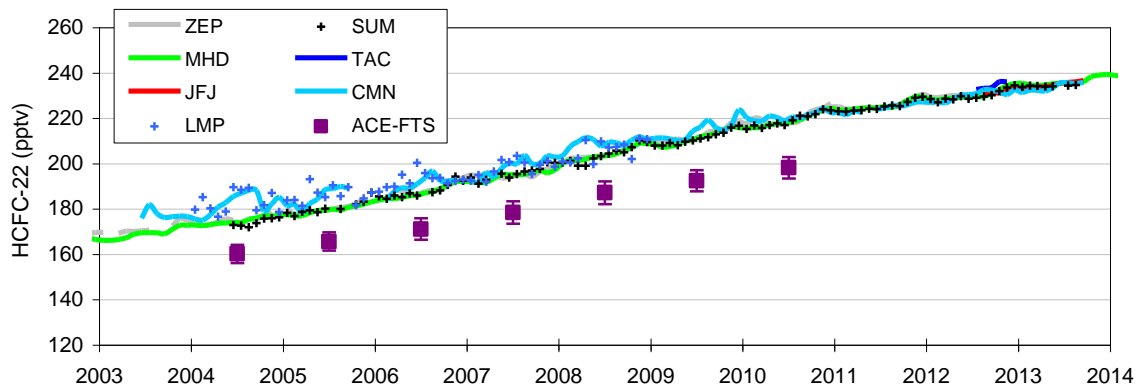


Fig. 12: Satellite-borne and *in situ* ground-level measurements of HCFC-22 at various stations across Europe. Crosses indicate non-continuous measurements (flask sampling). Purple squares represent annual averages obtained from satellites between 30 °N and 30 °S. Error bars indicate the median absolute deviation of annual averages.

Conclusions

Current *in situ* atmospheric measurements of ODS in Europe show consistent results and are sufficient to detect trends in ODS concentrations in Europe. Despite their much lower accuracy, measurements carried out by space-borne instrumentation (e.g. from satellites) show similar trends. The data interpretation and assimilation of space-borne measurements is much more complex and associated with higher uncertainties, but satellite data provide a global coverage, and interesting information of vertical profiles as well.

In general the trends of ODSs in Europe (in-situ ground level measurements), are similar to the trends in the rest of the world (see ref. [4] containing *in situ* ground level measurements, flask sampling and satellite observations), indicating the success of the Montreal Protocol.

However, the importance of N₂O as ozone depleting substance has not been fully considered yet. N₂O is indeed covered by the Kyoto protocol on greenhouse gases, but not by the Montreal Protocol on ODSs.

Another important issue needs further critical evaluation. ODS substitutes (e.g. fluorinated gases, HFC's) are also extremely powerful greenhouse gases like the CFC's/HCFC's. The replacement of ODS by these substitutes will therefore lead to a further increase of the greenhouse effect, if they are emitted in large amounts. The greenhouse effect warms up the troposphere, and cool down the stratosphere, while stratospheric ozone depletion is exacerbated by cold stratospheric temperature (see e.g. Daniel et al., 2010 [13]). The substitution of ODS by e.g. fluorinated gases could therefore slow down the recovery of the ozone layer through the climatic effect of these substitutes.

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<http://gaw.empa.ch/gawsis/> (GAWSIS: Global Atmospheric Watch Station Information System)

<http://ds.data.jma.go.jp/gmd/wdogg/wdogg.html> (WDCGG: World Data Centre for Greenhouse Gases).

<http://www.esrl.noaa.gov/gmd/> (NOAA (National Oceanic and Atmospheric Administration): Global Monitoring Division).

The 7 “European stations”:

- 1) Zeppelin (ZEP) station, Ny-Ålesund, Svalbard, Norway.
PI: Dr. Chris Lunder (chris.lunder@nilu.no).
Co-workers: Dr. O. Hermanson (oh@nilu.no), Dr. P.B. Krummel (Paul.Krummel@csiro.au) and Dr. Ray Wang (raywang@eas.gatech.edu).
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- 4) Tacolneston (TAC) station, UK.
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- 5) Jungfraujoch (JFJ) station, Switzerland.
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- 6) Monte Cimone (CMN) station, Italy.
PI: Prof. Michela Maione (michela.maione@uniurb.it).
- 7) Lampedusa (LMP) station, Italy.
PI: Dr. Alcide di Sarra (alcide.disarra@enea.it).

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- [3] <http://agage.mit.edu/>: *Webpage of project AGAGE (Advanced Global Atmospheric Gases Experiment).*
- [4] *World Meteorological Organization (WMO), Assessment for Decision-Makers: Scientific Assessment of Ozone Depletion: 2014, World Meteorological Organization, Global Ozone Research and Monitoring Project—Report No. 56, Geneva, Switzerland, 2014.*
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