



Anthropogenic changes of CO₂, CH₄, N₂O, CFCI₃, CF₂Cl₂, CCl₂FCCIF₂, CHCl₃, CH₃CCl₃, CCl₄, SF₆ and SF₅CF₃ mixing ratios in the atmosphere over southern Poland

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An overview of long-term, systematic observations of trace gas composition of the atmosphere over southern Poland is given. Three major greenhouse gases (CO₂, CH₄, N₂O) and selected halocarbons (freons F-11, F-12 and F-113; chloroform; 1,1,1-trichloroethane; carbon tetrachloride; sulphur hexafluoride and trifluoromethyl sulphur pentafluoride) were monitored. Measurements were performed at two locations of contrasting characteristics: (1) the high-mountain site Kasprowy Wierch, High Tatras, representing atmospheric conditions relatively free of local influences, and (2) two sites located in the Kraków agglomeration, representing a typical urban atmosphere. The data available for Kraków and Kasprowy Wierch were compared with the Mace Head data, representing a marine regional background. The impact of continental sources for some of the measured gases is clearly seen in the Kraków and Kasprowy Wierch records. The mean offset between CH₄ concentrations recorded at Kasprowy Wierch and at Mace Head for the period 1998–2012 is 20.7 ppb and stems from continental emissions of this gas originating mainly from anthropogenic activities (leaks of natural gas distribution networks, landfills, livestock). For N₂O, a similar offset of ca. 1 ppb for the period 2009–2012 was observed. Although the long-term concentration trends of selected halogenated compounds measured in Kraków coincide in general with the respective trends in Mace Head data, the Kraków records contain numerous spikes and periods of enhanced concentrations, reflecting the impact of local sources of these compounds. The impact of a legislative framework enforced in Poland in July 2002, regulating the trade, storage and disposal of ozone-depleting substances, is visible in the Kraków record of halogenated compounds.

Key words: atmosphere, monitoring, greenhouse gases, halogenated compounds.

INTRODUCTION

The atmosphere is a key component of the Earth's global ecosystem. It fulfills several important roles: (1) it contains gases essential for present forms of life on the Earth, (2) it shields the Earth's surface from harmful radiation in the form of cosmic rays and the UV portion of the solar spectrum, (3) it distributes the incoming solar energy between low and high latitudes, smoothing thermal contrasts between equatorial and polar regions, and, (4) through a natural greenhouse effect it provides comfortable temperatures for the Earth's biosphere. The present composition of the atmosphere is a result of long-term evolution encompassing the entire history of our planet. The at-

mospheric reservoir is linked to other major compartments of the global ecosystem via mass and energy fluxes, and responds to external and internal forcing.

Anthropogenic activities modify the composition of Earth's atmosphere in different ways. For instance, the concentrations of natural greenhouse gases such as carbon dioxide, methane and nitrous oxide have increased substantially over the past 150 years leading to additional heating of the Earth's surface. Moreover, purely anthropogenic gaseous trace substances present in the atmosphere, such as freons and SF₆, also act as powerful greenhouse gases and some of them exert an important control over the stratospheric ozone layer which plays a vital role in shielding Earth's surface from harmful UV radiation originating from the Sun. Finally, human activities introduce a great variety of other trace substances to the atmosphere, such as SO_x, NO_x, CO, dust, VOCs and many others, often leading to substantial deterioration of air quality with harmful consequences to human health.

It is therefore not surprising that the composition of Earth's atmosphere is being watched with increasing awareness on lo-

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cal, regional and global scales. This is done through regional and global monitoring networks such as Global Atmosphere Watch (www.wmo.int/pages/prog/gaw), the NOAA (National Oceanic and Atmospheric Administration) Earth Systems Research Laboratory (www.esrl.noaa.gov/gmd/) and the Advanced Global Atmospheric Gases Experiment (www.agage.eas.gatech.edu). Also new initiatives, such as the Integrated Carbon Observation System (www.icos-infrastructure.eu), are being launched. Such networks fulfill several functions. Firstly, they document the spatial and temporal evolution of the composition of Earth's atmosphere as a result of natural processes and human activities. Secondly, they help to assess the effectiveness of international agreements, such as the Kyoto Protocol or Montreal Protocol, aimed at reducing atmospheric concentrations of key trace substances influencing the radiative balance of Earth such as CO₂, CH₄, N₂O and SF₆, or depleting the stratospheric ozone layer (Freons, halogenated compounds). Finally, they provide valuable data for current research on the global carbon cycle ([Global Carbon Project, 2012](#)) and the behavior of various trace substances in the atmosphere (e.g., [Simmonds et al., 1998](#); [Prinn et al., 2000](#); [Fang et al., 2012](#); [Maione et al., 2013](#)). In addition to large-scale monitoring activities, many local networks are also in operation, providing ground-truth data for managers and politicians responsible for air quality issues in urban centers.

Here we present an overview of long-term, systematic observations of the trace gas composition of the atmosphere over southern Poland. Three major greenhouse gases (CO₂, CH₄, N₂O) and selected halocarbons [freons F-11 (CFCl₃), F-12 (CF₂Cl₂) and F-113 (CCl₂FCClF₂); chloroform (CHCl₃); 1,1,1-trichloroethane (CH₃CCl₃); carbon tetrachloride (CCl₄), sulphur hexafluoride (SF₆) and trifluoromethyl sulphur pentafluoride (SF₅CF₃)] were monitored. Measurements were performed at two locations of contrasting characteristics: (1) the high-mountain site Kasprowy Wierch, High Tatras, representing atmospheric conditions relatively free of local influences, and (2) two sites located in the Kraków agglomeration, representing a typical urban atmosphere ([Fig. 1](#)). The observations of CO₂ and CH₄ atmospheric mixing ratios at Kasprowy Wierch go back to 1994 while N₂O has been regularly measured there

since 2009. Regular measurements of halogenated compounds in the Kraków atmosphere started in 1997. The trace gas composition and trends in the atmosphere over southern Poland is discussed in the context of local emissions of these gases and is related to regional baseline data.

DESCRIPTION OF THE MONITORING SITES

The Kasprowy Wierch station (49°14'N, 19°59'E, 1989 m a.s.l., 300 m above the tree line) is situated on top of the Kasprowy Wierch peak in the Tatra Mountains, at the intersection of three main valleys at the border between Poland and Slovakia. The climate of the area is typical of a continental mountain location, with large diurnal and seasonal variations of temperature, high precipitation rates, frequent changes of atmospheric pressure, and strong winds. Local surface winds are controlled by the morphology of the surrounding area. Westerly winds are the dominant circulation feature in the lower troposphere. Since Kasprowy Wierch is situated within the transition zone between the free troposphere and the planetary boundary layer (PBL) and is relatively free of local influences, this site is considered a regional reference station for trace gas measurements in the lower atmosphere over Central and Eastern Europe. Since 1994, regular observations of atmospheric mixing ratios of CO₂ and CH₄ have been performed at this site ([Necki et al., 2003](#); [Chmura et al., 2008](#); [Necki et al., 2013](#)). From September 1994 till June 1996 weekly composite samples of air were collected and the CO₂ and CH₄ concentration was measured at the Institute of Environmental Physics, University of Heidelberg, Germany. From July 1996 onwards, quasi-continuous measurements using an automatic gas chromatograph were conducted at this site. In the following, only quasi-continuous measurements at this site are described and discussed.

Kraków belongs among the four largest cities in Poland. It is located approximately 100 km north of the Tatra Mountains. With about one million inhabitants, rapidly growing car traffic and significant industrial activities, the Kraków agglomeration represents a typical urban environment in eastern Europe. The



Fig. 1. Locations of long-term monitoring sites for trace gas composition of the atmosphere over southern Poland the high-mountain station Kasprowy Wierch (KW), located in the Tatra Mountains, and station A (AGH University campus) and station B (Institute of Nuclear Physics), both located in the Kraków agglomeration (KR)

city is located in the Vistula River valley which is oriented in this region along an east-west axis. To the south, the city borders hilly terrain, while to the north it opens towards a flat upland area. In addition, with prevailing westerly circulation, the Kraków region is under substantial influence of a large coal mining and industrial district (Upper Silesia) located approximately 60 km west of the city. Characteristic features of the local climate are generally weak winds (annual average around 2.7 m s⁻¹) and frequent inversions, extending sometimes over several days, particularly during winter seasons. These factors favour accumulation of gases originating from surface emissions in the atmosphere of the city.

The monitoring site A (Fig. 1; 50°04'N, 19°55'E, 220 m a.s.l.) is situated on the University campus located in the western part of the city, bordering recreation and sports grounds. The air intake is placed on the roof of the Faculty building, approximately 20 metres above the local ground. In addition to measurements of atmospheric CO₂ and CH₄ mixing ratios, seven halogenated compounds (CFCl₃, CF₂Cl₂, CCl₂FCClF₂, CHCl₃, CH₃CCl₃, CCl₄, SF₆) were also measured at this site between July 1997 and May 2005. Starting from November 2005 these gases have been monitored at site B (50°05'N, 19°53'E, 233 m a.s.l.) located on the campus of the Institute of Nuclear Research, Polish Academy of Science, approximately 3.5 km north-west of site A (Fig. 1). In addition, several measurement campaigns aimed at quantification of atmospheric mixing ratios of SF₅CF₃ have been conducted at site A between 2001 and 2012.

METHODS

Regular measurements of the trace gas composition of the atmosphere over southern Poland were performed with the aid of gas chromatography techniques. Atmospheric mixing ratios of carbon dioxide and methane are measured at Kasprowy Wierch and in Kraków using automatic gas chromatographs (Hewlett Packard 5890 and Agilent 6890N, respectively) equipped with a flame ionization detector (FID), a 3 m column (Porapak QS) and nickel catalyst converting carbon dioxide to methane (Necki et al., 2003). Nitrous oxide is measured at Kasprowy Wierch using an electron capture detector (ECD) and double-column system configured in a back-flush mode (2 m pre-column Hysep Q 80/100 and 4 m analytical column Hysep Q 80/100). This analytical set-up allows the measurement of carbon dioxide, methane and nitrous oxide in a quasi-continuous mode, with consecutive measurements performed every 15–30 minutes. The measurements are conducted in a sequence standard–sample–standard. Each working standard is calibrated against two reference gases certified by NOAA Earth Systems Research Laboratory, which provide a direct connection to the internationally recommended scales for all three measured gases. The following scales are used: WMO (World Meteorological Organization) X2007 for CO₂, NOAA 2004 for CH₄ and NOAA 2006A for N₂O. In addition, both sites have been participating in the Cucumbers intercomparison program (www.cucumbers.uea.ac.uk) in which calibrated gas standards of near-atmospheric concentrations are periodically measured by research groups throughout Europe in order to ensure adequate measurement intercomparability.

Measurements of halogenated compounds were conducted using a two-channel gas chromatograph (GC Fisons, type 8000), equipped with electron capture detectors (ECD) working in a constant current mode (Lasa and Sliwka, 2001). In each channel, two columns working in a back-flush mode are used. In the first channel equipped with two stainless steel columns (filling: 10% SP 2100, 80/100 mesh, length 0.6 and 3 m,

respectively) F-11, F-113, CHCl₃, CH₃CCl₃ and CCl₄ are analysed, while the second channel (stainless steel columns; filling: molecular sieve 5A, 80/100 mesh; length 1 and 3 m, respectively) is devoted to analysis of SF₆ and freon F-12. The working temperature of the columns is 55°C and the temperature of the detectors in both channels is 300°C. The measurements are performed in the sequence: standard–sample–standard. The concentrations of the compounds measured are calculated using the five-point Lagrange interpolation method (Śliwka and Lasa, 2002). The measurements are calibrated against a primary standard prepared in 1996 at the Scripps Oceanography Institute, San Diego, USA. The primary standard was recalibrated in January 2013 and the measured concentrations of the trace gases of interest were transferred to the SIO 2005 scale.

Measurements of atmospheric SF₅CF₃ mixing ratios were performed by gas chromatography coupled with custom-built cryogenic pre-concentration unit. For every analysis, 200 ml of air passed through a trap cooled down to –110°C, on which the compounds with boiling points higher than the temperature of the trap are adsorbed. Agilent 6890N with 8m At-1000 on Carbograph and 1m Molsieve 5A column at 65°C in back-flush mode is used to separate SF₅CF₃ from other compounds. A standard -ECD detector heated to 350°C and working in constant current mode is applied to determine the mixing ratios of the measured gas. Injection of the adsorbed gases to the GC system is done through imposing a high current on the cryo-trap, thus leading to a sharp increase in the temperature of the unit and release of the adsorbed gases. The analyses of SF₅CF₃ mixing ratios were performed on flask samples collected in Kraków, typically at noon hours, when vertical mixing of the local atmosphere is the most intense, while at Kasprowy Wierch the flasks were collected during night hours, when the station was sampling free troposphere. The measurements were calibrated against three primary standards which have been inter-calibrated by two laboratories which currently perform this type of measurements: USGS, Reston, USA and the University of East Anglia, Norwich, UK.

Table 1 summarizes two key parameters characterizing the quality of the analytical systems used to measure atmospheric mixing ratios of the trace constituents of the local atmosphere. The Limit of Detection (LOD) was quantified for each the analysed compounds as a double amplitude of the noise of the analytical system in use, while the External Reproducibility (ER) was quantified as a standard deviation of a single measurement for repeated analyses of working standards containing ambient concentrations of the trace gases analysed.

RESULTS AND DISCUSSION

CHANGES IN TRACE GAS COMPOSITION OF THE ATMOSPHERE OVER SOUTHERN POLAND

The region of southern Poland where the monitoring sites are located is characterized by a relatively high degree of urbanization. Although the Kasprowy Wierch site was selected to minimize the impact of local sources of greenhouse gases, it has been demonstrated that anthropogenic CO₂ emissions from Zakopane town can be traced in the record of atmospheric mixing ratios of this gas available for the site (Necki et al., 2013). Also, the impact of the Upper Silesia region, with its heavy industry, 19 interconnected cities with approximately 3.5 million inhabitants and 29 active coal mines, can be traced in the Kasprowy Wierch record.

Table 1

Limit of Detection (LOD) and External Reproducibility (ER) of the analytical systems in use to measure ambient concentrations of the selected trace gases in the atmosphere of southern Poland

Compound	LOD ^a	ER ^a
Carbon dioxide (CO ₂)	0.05 ± 0.03 ppm	0.1 ppm
Methane (CH ₄)	6.3 ± 0.5 ppb	2.0 ppb
Nitrous oxide (N ₂ O)	1.3 ± 0.3 ppb	0.4 ppb
Freon F-11 (CFCl ₃)	1.2 ± 0.7 ppt	4.8 ppt
Freon F-12 (CF ₂ Cl ₂)	5.7 ± 2.6 ppt	6.4 ppt
Freon F-113 (CCl ₂ FCFCl ₂)	6.2 ± 0.9 ppt	1.8 ppt
Chloroform (CHCl ₃)	16.2 ± 2.7 ppt	1.7 ppt
1,1,1-trichloroethane (CH ₃ CCl ₃)	6.7 ± 0.9 ppt	1.5 ppt
Carbon tetrachloride (CCl ₄)	2.9 ± 0.6 ppt	1.0 ppt
Sulphur hexafluoride (SF ₆)	0.15 ± 0.08 ppt	0.2 ppt
Trifluoromethyl sulphur pentafluoride (SF ₅ CF ₃)	2.1 ± 0.7 ppq	2.5 ppq

a – see text for definition

In the following, the atmospheric trace gas concentrations measured at Kasprowy Wierch and in Kraków are described and compared with the data available for the Mace Head station located in western Ireland (53°20'N, 9°54'W). The Mace Head record is considered a marine background reference for the European continent. Selection of two monitoring sites with contrasting characteristics (urban versus remote, relatively clean environment) allows demonstration of the impact of urbanized areas on the trace gas composition of the local atmosphere.

CARBON DIOXIDE

Figure 2 shows the atmospheric CO₂ mixing ratio record available for the Kasprowy Wierch station. Shown are daily means of the measured mixing ratios, calculated after appropriate data selection procedure. A three-step procedure was ap-

plied to select the data representing background conditions at the station (Necki et al., 2003). Daily mean values were further smoothed using the routine recommended by NOAA (CCGvu 4.40; Thoning et al., 1989). For comparison, the CO₂ trend curve representing the regional marine background (Mace Head) is also shown (<http://www.esrl.noaa.gov/gmd/>; GLOBALVIEW-CO₂, 2013). The annual means, seasonal amplitudes and growth rates of the CO₂ mixing ratios measured at Kasprowy Wierch are summarized in Table 2. The annual means are arithmetic averages of the daily mean values. The amplitudes of seasonal variations were calculated using the CCGvu 4.40 routine (Thoning et al., 1989) which uses the smoothed CO₂ record. The annual growth rates were calculated through derivation of the trend curve shown in Figure 2.

The concentration of carbon dioxide at Kasprowy Wierch has increased by 9%, from 361.4 ppm in 1997 to 394.0 ppm in

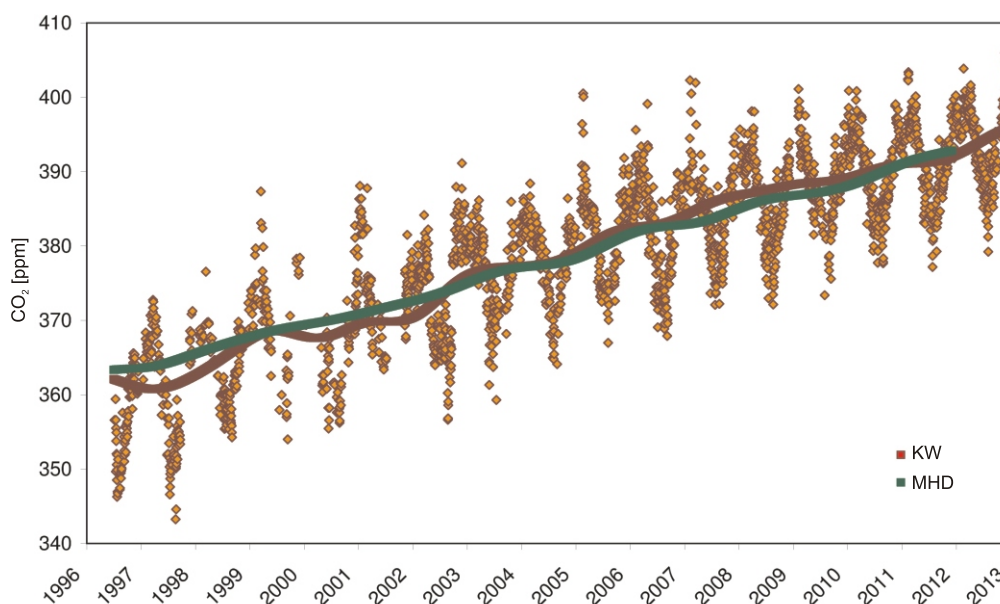


Fig. 2. The record of CO₂ mixing ratios available for the Kasprowy Wierch station

Shown are daily means calculated on the basis of individual gas chromatographic measurements, after appropriate data selection procedure; the trend curves for Kasprowy Wierch (KW) and Mace Head (MHD) data are also shown; the trend curve for Mace Head has been calculated on the basis of monthly mean CO₂ mixing ratios at this station (<http://www.esrl.noaa.gov/gmd/>; GLOBALVIEW-CO₂, 2013)

Table 2

Basic characteristics of the CO₂ record available for the Kasprowy Wierch station

Year	Carbon dioxide		
	Annual average [ppm]	Amplitude [ppm]	Growth rate [ppm y ⁻¹] ^a
1997	361.4	19.1	1.7
1998	364.9	15.6	4.7
1999	369.4	19.1	0.5
2000	367.0	19.5	1.6
2001	370.0	20.8	0.9
2002	373.7	18.4	5.6
2003	376.3	12.6	1.3
2004	377.7	16.4	1.7
2005	381.1	16.4	3.4
2006	382.6	17.9	1.6
2007	386.0	18.6	2.8
2008	387.2	15.1	1.4
2009	388.7	18.3	0.9
2010	390.4	13.4	1.9
2011	391.2	15.1	1.1
2012	394.0	13.1	3.8

a – calculated on the basis of the trend curve shown in Figure 2 (see text)

2012 (Table 2). A distinct seasonal cycle of CO₂ concentrations is clearly seen in Figure 2, with high values in winter and low values in summer. This cycle is driven by the seasonal character of photosynthetic activity of the biosphere. The peak-to-peak

amplitude of the seasonal fluctuations of CO₂ mixing ratios varied in the period discussed between 12.6 ppm (2003) and 20.8 ppm (2001). The low amplitude recorded in 2003 can be attributed to a very hot summer in this particular year in Europe, reducing photosynthetic activity of the regional biosphere (Ciais et al., 2005). There has also been a reduction of the CO₂ amplitude in the recent years (2010–2012). The growth rate of CO₂ concentration varied significantly over the period discussed: the maximum (5.6 ppm year⁻¹) was observed in 2002 while the minimum (0.5 ppm year⁻¹) was recorded in 1999. The trend curves for the Kasprowy Wierch and Mace Head data are very similar, particularly for the last decade.

METHANE

Figure 3 shows the atmospheric CH₄ record available for the Kasprowy Wierch station. As for CO₂ (Fig. 2), shown are daily means of the measured mixing ratios, calculated after data selection analogous to that applied to the CO₂ data. The daily mean values were further smoothed using the routine recommended by NOAA (CCGvu 4.40; Thoning et al., 1989). For comparison, the CH₄ trend curve representing the regional marine background (Mace Head) is also shown (<http://www.esrl.noaa.gov/gmd/>; GLOBALVIEW-CH₄, 2009). The annual means and annual growth rates of CH₄ mixing ratios recorded at Kasprowy Wierch, as well as the mean annual offsets between the Kasprowy Wierch and Mace Head stations, calculated for the period 1997–2012, are shown in Table 3.

The concentration of methane at Kasprowy Wierch has increased from 1843 ppb in 1997 to 1889 ppb in 2012. By contrast to CO₂, seasonal cycle is not present in the data. The long-term trend in the data is generally more variable than is case with CO₂; the annual growth rates vary from –32.9 ppb year⁻¹ in 2003 to +15.1 ppb year⁻¹ in 2007. The origin of anomalously high CH₄ concentrations recorded at Kasprowy Wierch in

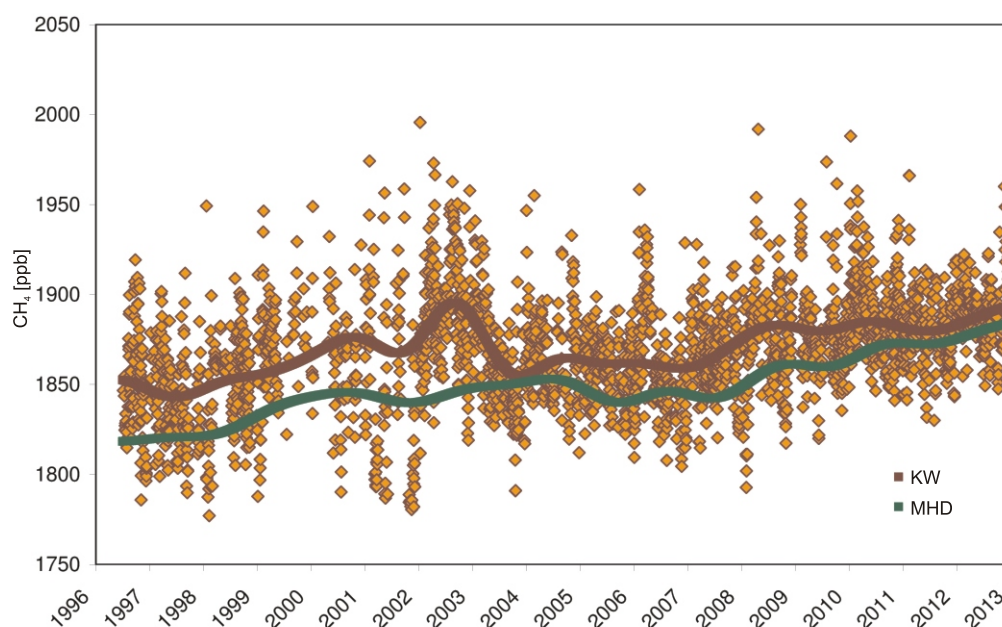


Fig. 3. The record of CH₄ mixing ratios available for the Kasprowy Wierch station

Shown are daily means calculated on the basis of individual gas chromatographic measurements, after appropriate data selection procedure; the trend curves for Kasprowy Wierch (KW) and Mace Head (MHD) data are also shown; the trend curve for Mace Head has been calculated on the basis of flask data representing the marine sector only (<http://www.esrl.noaa.gov/gmd/>; GLOBALVIEW-CH₄, 2009)

Table 3

Basic characteristics of the CH₄ record available for the Kasprowy Wierch station

Year	Methane		
	Annual average [ppb]	Growth rate ^a [ppb y ⁻¹]	Offset KW–MHD ^b [ppb]
1997	1842.9	0.3	23.9
1998	1852.7	8.1	26.5
1999	1864.2	10.8	21.2
2000	1869.9	9.0	28.0
2001	1866.1	-0.7	28.8
2002	1894.0	13.7	44.9
2003	1862.9	-32.9	16.9
2004	1865.7	8.8	9.6
2005	1859.0	-2.1	19.5
2006	1859.9	-2.5	15.7
2007	1868.8	15.1	21.7
2008	1878.1	9.3	24.1
2009	1882.6	0.1	20.0
2010	1886.3	-2.4	14.4
2011	1879.5	1.1	7.5
2012	1889.0	11.0	8.5

a – calculated on the basis of the trend curve shown in Figure 3; b – offset between the CH₄ trend curves for the Kasprowy Wierch (KW) and Mace Head (MHD) stations (cf. Fig. 3)

2002 is unclear and needs to be further investigated. Such an increase of CH₄ concentration was not observed at other CH₄ monitoring stations across Europe.

It is clear from Figure 3 that concentrations of CH₄ recorded at Kasprowy Wierch are shifted towards higher levels with respect to the Mace Head data. The offset varies between 7.5 ppb in 2011 to 44.9 ppb in 2002. Both CH₄ trend curves run roughly parallel, although an apparent reduction of the KW–MHD offset is visible in recent years (cf. Table 3). After stagnation during the period 2001–2007, the atmospheric concentrations of CH₄ have begun to increase again. This is a world-wide phenomenon, attributed to an increase in surface emissions of methane, mainly by wetlands in tropical south America and in boreal Eurasia (Bousquet et al., 2011). Higher concentrations of CH₄ recorded at Kasprowy Wierch when compared to the Mace Head data are due to continental emissions of methane and gradual loading of the air masses with CH₄ on their way from the Atlantic coast towards the centre of the continent.

NITROUS OXIDE

Regular measurements of atmospheric N₂O concentrations began at the Kasprowy Wierch station in January 2009. The N₂O record available to date is shown in Figure 4 and compared with the Mace Head regional marine reference record (<http://agage.eas.gatech.edu>; Prinn et al., 1990). Daily mean values of N₂O concentration are shown for both sites. It is apparent from Figure 4 that, as in case of CH₄, the continental emissions of this gas result in an apparent offset of Kasprowy Wierch N₂O data with respect to the Mace Head data. The difference is of the order of 1 ppb. Seasonal variations of N₂O mixing ratios, with N₂O maxima in winter and early spring and minima during summer and early autumn, are clearly seen in the Mace Head record. It has been suggested that the seasonality

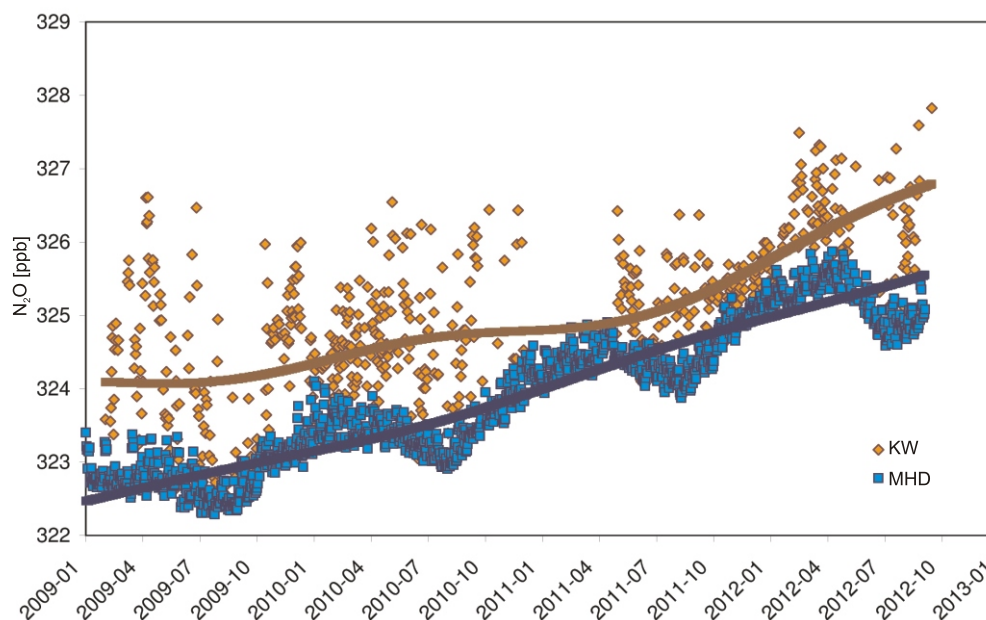


Fig. 4. The record of N₂O mixing ratios available for the Kasprowy Wierch station

Shown are daily means (orange) calculated on the basis of individual gas chromatographic measurements after appropriate data selection procedure; the blue squares represent daily means of N₂O mixing ratios measured at Mace Head (<http://agage.eas.gatech.edu/>; Prinn et al., 1990); the trend curves for Kasprowy Wierch (KW) and Mace Head (MHD) data are also shown

of N₂O concentration seen at Mace Head might be attributed to the seasonal impact of the stratosphere (Levin et al. 2002; Jiang et al., 2007). Although this seasonality is not well-pronounced in the Kasprowy Wierch record, it can be noted that the minima of N₂O concentrations recorded at this station closely follow the seasonality of N₂O signal seen in the Mace Head record.

HALOCARBONS

Figure 5 summarizes the measurements of selected halogenated compounds in the atmosphere over southern Poland, carried out during the period 1997–2012. Daily mean values of CFC₃, CF₂Cl₂, CCl₂FCClF₂, CHCl₃, CH₃CCl₃, CCl₄ and SF₆ are shown in Figure 5A–G. They were calculated as arithmetic averages of individual measurements. Shown also are trend curves (red) derived from daily means of these compounds measured at the Mace Head station representing the regional marine background (<http://agage.eas.gatech.edu>; Fraser et al., 1996; Cunold et al., 1997; Simmonds et al., 1998; Prinn et al., 2000; O'Doherty et al., 2001; Reimann et al., 2005), calculated using the CCGvu 4.40 routine (Thoning et al., 1989). Figure 5H shows the atmospheric concentrations of SF₅CF₃ measured in flask samples collected in Kraków and at Kasprowy Wierch. The trend curve shown in Figure 5H represents a polynomial fit of the data shown in Figure 5H, including also all other atmospheric SF₅CF₃ data published up to now (Sturges et al., 2000, 2012; Rosiek et al., 2007; Busenberg and Plummer, 2008; Erboy and Smethie, 2012). Annual means of the daily mean values of CFC₃, CF₂Cl₂, CCl₂FCClF₂, CHCl₃, CH₃CCl₃, CCl₄ and SF₆ measured in Kraków during the period 1998–2012 are summarized in Table 4.

It is apparent from Figure 5A–G that the measured trace compounds generally follow a decreasing trend which is particularly pronounced for CH₃CCl₃ (Śliwka et al., 2010). The only exception is sulphur hexafluoride which reveals a linear increase, in accordance with the increasing concentrations of this gas observed in other parts of the world (Levin et al., 2010). Although the measured mixing ratios of the compounds analysed generally follow the long-term trends in marine atmosphere represented by the Mace Head data, numerous spikes and periods of elevated concentrations of these compounds are evident in the Kraków record. For instance, anomalously high concentrations of CCl₄, CHCl₃ and F-113 were observed in Kraków during 2000 and 2001. Also, isolated spikes exceeding the background values by a factor of ten or higher occurred frequently, the most prominent example being the concentration of 1836 ppt of CHCl₃ recorded on September the 3th, 1998, to be compared with typical concentrations of this gas in the Kraków atmosphere around that time of the order of 100 ppt. As CHCl₃ and CCl₄ are used as solvents in dry cleaning facilities, the impact of near-by sources is quite probable. Other prominent spikes are present also in the records of F-12 and CCl₄.

It is also apparent from Figure 5 that for majority of the halocarbons analysed, the atmospheric mixing ratios measured became less noisy after 2002. This is particularly the case with CHCl₃, CCl₄ and CH₃CCl₃. The reduction of short-term variability coincides with enforcing in Poland of the law regulating the trade, storage and disposal of ozone-depleting substances, following the Montreal Protocol, which took place in July 2002. The substances measured, except SF₆ and SF₅CF₃, belong to this group.

Daily variations of trace atmospheric constituents measured close to the ground are controlled by two main factors: (1)

intensity of vertical mixing of the lower atmosphere, and (2) the strength of the local sources of these constituents. Vertical mixing of the lower atmosphere is often modulated on a daily time scale by night-time inversions suppressing vertical mixing during night hours. In contrast, most intense vertical mixing occurs typically around noon and the early afternoon hours. If the surface emissions of the trace constituents measured are roughly constant on a daily time scale, their concentrations in the near-ground atmosphere will be largely controlled by changing mixing conditions of the lower atmosphere (see next section). The emissions of halogenated compounds measured in the framework of this study typically have far more complex temporal characteristics than, for instance, CO₂ or CH₄. Consequently the concentrations of these compounds measured in the near-ground atmosphere usually do not reveal distinct daily variations.

To quantify the average load of the local atmosphere in Kraków with respect to the halocarbons measured, the records of their daily mean values shown in Figure 5A–G have been smoothed using the CCGvu 4.40 routine (Thoning et al., 1989) and offsets between the calculated trend curves for Kraków and Mace Head station were calculated. The annual mean offsets for the halocarbons measured are summarized in Table 5.

IMPACT OF URBAN ENVIRONMENT ON THE LOCAL ATMOSPHERE

Numerous sources of trace gas emissions are present in urbanized areas. For instance, local transport and heating systems release significant amounts of CO₂ related to the burning of fossil fuels. Globally, the emissions of carbon dioxide from fossil-fuel burning and cement production have increased by about 54%, from 6.2 PgC in 1990 to 9.5 PgC in 2011 (Quéré et al., 2013). Urbanized regions are also significant emitters of methane which leaks from gas distribution networks and local landfills.

Figure 6 shows an example of daily variations in CO₂ and CH₄ mixing ratios measured at Kasprowy Wierch and in Kraków during May 2004. Distinct daily variations of the measured concentrations are seen in the Kraków record, with increase in CO₂ and CH₄ concentrations during night hours and reduction during daytime. As indicated above, vertical mixing of the lower atmosphere is often significantly reduced during night by build-up of an inversion layer, thus leading to accumulation of trace compounds emitted from the surface. As seen in Figure 6, local enhancements of CO₂ and CH₄ in the Kraków atmosphere during night hours can be substantial; in the record shown, concentrations exceeding the baseline level by ca. 60% were recorded. At Kasprowy Wierch such daily fluctuations are much weaker and are shifted in-phase, with the minima during night-time and the maxima during early afternoon (Necki et al., 2003).

Figure 7 shows a comparison of SF₆ mixing ratios measured at Kasprowy Wierch and in Kraków during the period 2011–2012. The data points represent flask samples collected at both sites. At Kasprowy Wierch site the samples were collected during night hours (2–4 a.m.) when the free troposphere is sampled by the station and the data represent regional background conditions (Necki et al., 2003). In Kraków, sampling was typically done during midday when vertical mixing of the local atmosphere is the most intense. It is clear from Figure 7 that the larger variability and enhanced SF₆ levels recorded in Kraków have their origin in local sources of this gas associated either with the Kraków agglomeration or with the industrialized region of Upper Silesia.

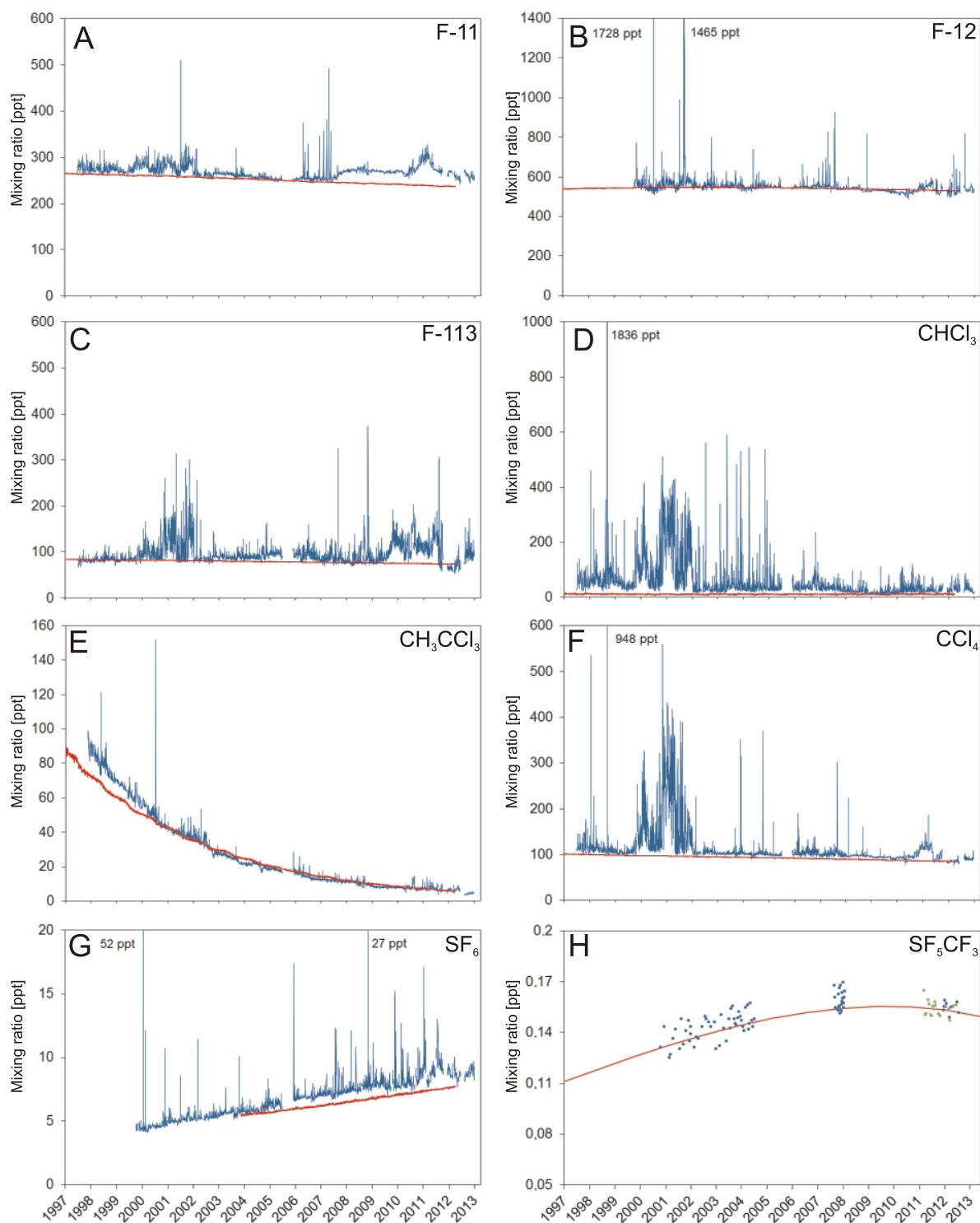


Fig. 5. The records of daily mean atmospheric mixing ratios of selected halocarbons measured in Kraków during the period 1997–2012

A–G – blue line, compared with the trend curve (red line) representing daily mean Mace Head data (<http://agage.eas.gatech.edu>; Fraser et al., 1996; Cunnold et al., 1997; Simmonds et al., 1998; Prinn et al., 2000; O'Doherty et al., 2001; Reimann et al., 2005); **H** – SF₅CF₃ mixing ratios measured at Kasprowy Wierch (green points) and in Kraków (blue points); the trend curve (red line) represents a polynomial fit of the data shown in Figure 5H, including also all other atmospheric SF₅CF₃ data published up to now (Sturges et al., 2000, 2012; Rosiek et al., 2007; Busenberg and Plummer, 2008; Erboy and Smethie, 2012)

Table 4

The annual mean concentrations of the selected halogenated compounds measured in Kraków during the period 1998–2012

Year	Concentration [ppt]						
	F-11	F-113	CHCl ₃	CH ₃ CCl ₃	CCl ₄	SF ₆	F-12
1998	274.7	84.6	106.6	78.6	116.5	–	–
1999	274.8	85.7	65.4	63.1	112.0	4.42	572.5
2000	279.6	105.2	136.2	49.5	175.0	4.77	554.7
2001	283.8	122.8	173.9	39.5	188.2	5.11	588.8
2002	265.2	90.7	39.1	32.8	106.6	5.31	556.1
2003	263.8	89.5	50.5	25.0	104.5	5.68	554.2
2004	257.9	91.6	47.5	20.6	104.0	5.93	549.0
2006	255.9	93.8	42.8	14.4	104.9	6.91	551.5
2007	262.8	87.4	34.1	12.0	102.2	7.29	558.5
2008	272.2	86.9	23.9	10.5	98.2	7.70	539.4
2009	269.4	98.6	18.6	8.2	93.6	7.91	529.2
2010	274.7	115.1	30.6	7.8	9.7	8.15	524.8
2011	283.6	110.7	26.8	7.4	104.8	9.07	542.5
2012	260.7	83.1	32.8	5.6	87.9	8.72	536.7

Table 5

The annual mean offsets between smoothed concentration records of selected halocarbons measured in Kraków and at Mace Head station (KR–MHD)

Year	Concentration difference (ppt)						
	F-11	F-113	CHCl ₃	CH ₃ CCl ₃	CCl ₄	SF ₆	F-12
1998	10.7	1.2	83.0	12.4	15.5	–	–
1999	14.4	3.5	62.0	7.8	16.0	–	20.9
2000	19.7	22.8	128.3	3.1	82.0	–	9.7
2001	22.5	37.9	150.5	0.9	88.1	–	35.7
2002	10.7	13.9	34.8	0.6	9.6	–	16.2
2003	8.5	8.7	35.6	–2.3	10.3	0.2	6.1
2004	4.9	12.8	36.6	–1.9	11.2	0.4	4.9
2006	8.1	15.9	33.2	–1.3	12.8	0.8	8.7
2007	16.4	10.1	23.8	–1.2	12.0	0.9	16.7
2008	27.9	8.4	12.2	–0.6	9.5	1.1	0.8
2009	25.6	23.3	8.7	–1.0	5.2	1.1	–8.6
2010	35.9	42.1	17.8	0.0	12.4	1.1	–6.3
2011	41.8	28.8	18.2	0.8	16.1	1.5	12.2
2012	23.0	6.5	18.7	–0.3	2.5	1.1	9.6

CONCLUSIONS

Long-term, systematic observations of three major greenhouse gases (CO₂, CH₄, N₂O) and selected halogenated compounds (F-11, F-12, F-113, CHCl₃, CH₃CCl₃, CCl₄ and SF₆) in the atmosphere over southern Poland allowed a deeper insight into the processes controlling the levels of these gases in the continental atmosphere at different time scales. Comparison of the trace gas composition of marine air masses entering the European continent, represented by the Mace Head data, with the atmospheric mixing ratios of these gases measured in the centre of the continent, some 1600 km from the Atlantic coast, helps to quantify the impact of continental sources of these

gases on the composition of the near-ground atmosphere in Central and Eastern Europe.

While the imprint of continental emissions on the measured values of the CO₂ mixing ratio is clearly visible on a seasonal time scale (the average peak-to-peak amplitude of seasonal fluctuations of CO₂ concentration is ca. 14.9 ppm for Mace Head, and increases to ca. 16.8 ppm for the Kasprowy Wierch site) reflecting the impact of seasonal activity of the continental biosphere, the long-term CO₂ trends for those two stations almost coincide. A different situation is observed for methane and nitrous oxide. The weak seasonality of CH₄ and N₂O records observed at Mace Head is barely seen in the centre of the continent. At the same time, a distinct offset between long-term trends of CH₄ concentrations measured at Mace Head and Kasprowy Wierch can be observed. The mean value of CH₄ offset for the period 1998–2012 is 20.7 ppb and originates from continental emissions of this gas resulting mainly from anthropogenic activities (leaks of natural gas distribution networks, landfills, livestock). For N₂O a similar offset in the order of 1 ppb for the period 2009–2012 is observed.

Comparison of quasi-continuous measurements of CO₂ and CH₄ mixing ratios performed in the urban atmosphere of Kraków and at the high-mountain site Kasprowy Wierch, located approximately 100 km apart, allows a deeper insight into the mechanisms controlling daily variations of atmospheric concentrations of these gases at both sites. Development of a nocturnal inversion layer in the atmosphere above the city leads to local enhancements of CO₂ and CH₄ concentrations in the Kraków atmosphere during night hours, significantly exceeding the baseline level. This concerns all gases which have surface emission sources operating all the time within the footprint of the given measurement site. Daily fluctuations of CO₂ and CH₄ mixing ratios recorded at Kasprowy Wierch are shifted in-phase (daily maxima and nocturnal minima) and are much weaker than in Kraków. They are related to local circulation of the atmosphere, bringing air from the surrounding valleys to the station during daytime. During the night, the station is often situated above the nocturnal inversion layer.

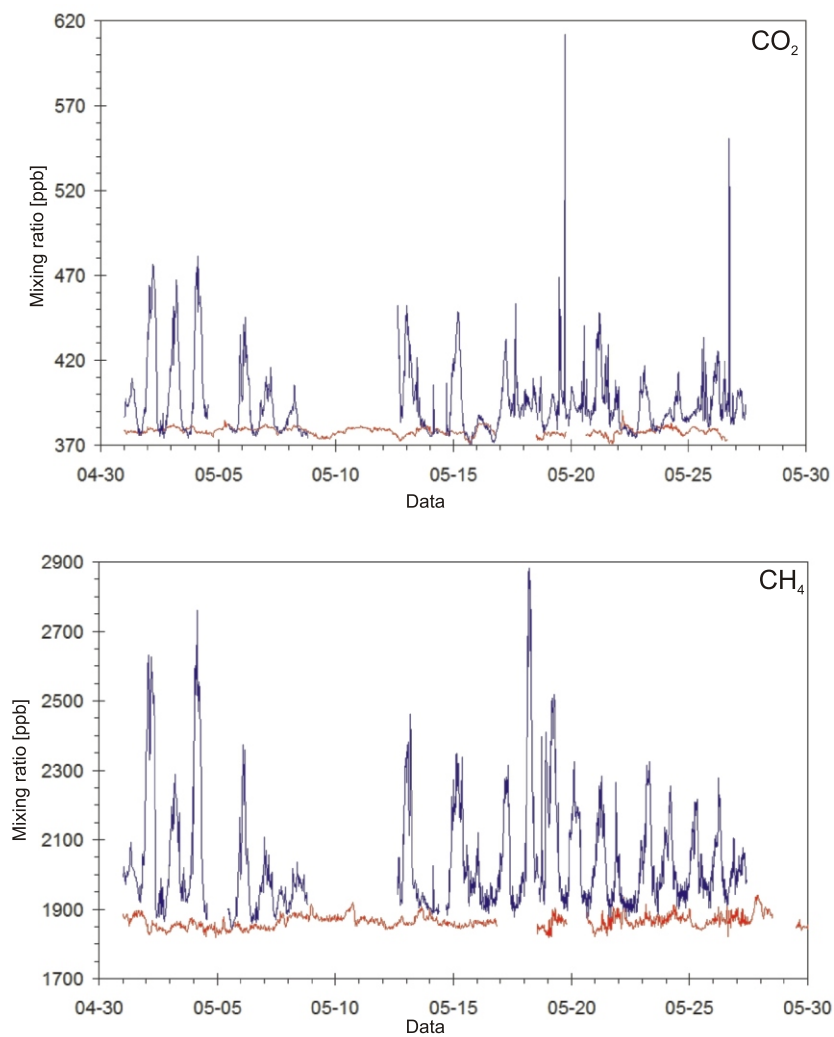


Fig. 6. Daily variations of CO_2 and CH_4 mixing ratios, observed in Kraków (blue) and Kasprowy Wierch (red) during May 2004

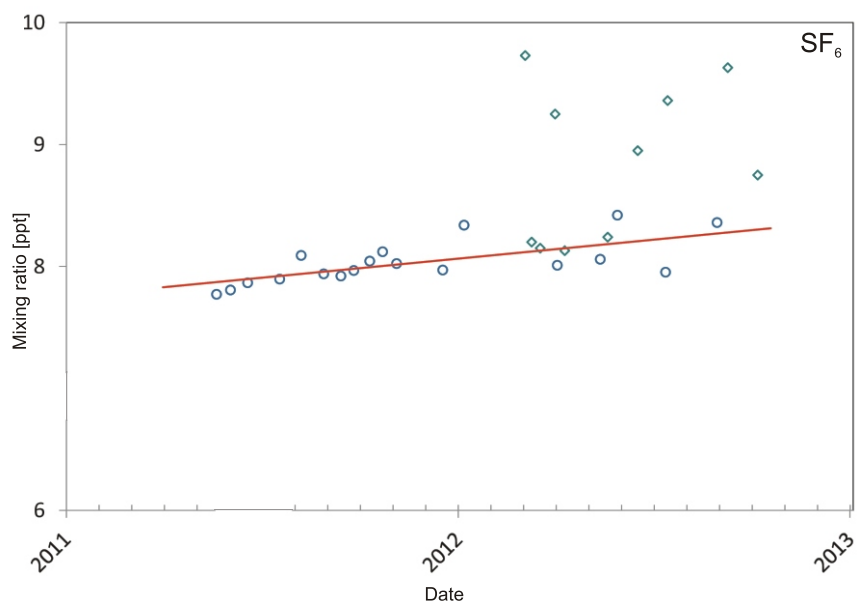


Fig. 7. Comparison of atmospheric SF_6 mixing ratios measured in flask samples collected in Kraków (green diamonds) and at Kasprowy Wierch (blue circles)

The line is the best fit line of the Kasprowy Wierch data

Although the long-term trends in concentrations of halocarbons measured in Kraków coincide in general with the respective trends seen in the Mace Head data, the Kraków records are characterized by numerous spikes and periods of enhanced concentrations, reflecting the impact of various local and/or regional sources of these compounds. As in the case of methane and nitrous oxide, this impact is reflected in the apparent offset between the concentrations of these compounds measured in Kraków and at Mace Head. Interestingly, the concentration records for the group of halocarbons which belong to ozone-depleting substances, reflects also the impact of legislative framework enforced in Poland in July 2002, aimed at regulating trade, storage and disposal of those substances, following the Montreal Protocol. The respective records became less noisy after that date.

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REFERENCES

- Bousquet, P., Ringeval, B., Pison, I., Dlugokencky, E.J., Brunke, E.-G., Carouge, C., Chevalier, F., Fortems-Cheiney, A., Frankenberg, C., Hauglustaine, D.A., Krummel, P.B., Langenfelds, R.L., Ramonet, M., Schmidt, M., Steele, L.P., Szopa, S., Yver, C., Viovy, N., Ciais, P., 2011. Source attribution of the changes in atmospheric methane for 2006–2008. *Atmospheric Chemistry and Physics*, **11**: 3689–3700.
- Busenberg, E., Plummer, L.N., 2008. Dating groundwater with trifluoromethyl sulfurpentafluoride (SF₅CF₃), sulfur hexafluoride (SF₆), CF₃Cl (CFC-13) and CF₂Cl₂ (CFC-12). *Water Research*, **44**: W02431, 1–18.
- Ciais, P., Reichstein, M., Viovy, N., Granier, A., Ogee, J., Allard, V., Aubinet, M., Buchmann, N., Bernhofer, Chr., Carrara, A., Chevalier, F., Noblet, N., de, Friend, A.D., Friedlingstein, P., Grünwald, T., Heinesch, B., Keronen, P., Knohl, A., Krinner, G., Loustau, D., Manca, G., Matteucci, G., Miglietta, F., Ourcival, J.M., Papale, D., Pilegaard, K., Rambal, S., Seufert, G., Soussana, J.F., Sanz, M.J., Schulze, E.D., Vesala, T., Valentini, R., 2005. Europe-wide reduction in primary productivity caused by the heat and drought in 2003. *Nature*, **437**: 529–533.
- Chmura, L., Rozanski, K., Necki, J.M., Zimnoch, M., Korus, A., Pycia, M., 2008. Atmospheric concentration of carbon dioxide in Southern Poland: comparison of mountain and urban environments. *Polish Journal of Environmental Studies*, **17**: 859–867.
- Cunnold, D.M., Weiss, R.F., Prinn, R.G., Hartley, D.E., Simmonds, P.G., Fraser, P.J., Miller, B.R., Alyea, F.N., Porter, L., 1997. GAGE/AGAGE measurements indicating reduction in global emissions of CCl₃F and CCl₂F₂ in 1992–1994. *Journal of Geophysical Research*, **102**: 1259–1269.
- Erboj, Y., Smethie, W.M., 2012. Trifluoromethyl sulfur pentafluoride and its relationship to sulfur hexafluoride and chlorofluorocarbon-12 in the atmosphere near the New York City metropolitan area. *Atmospheric Environment*, **35**: 135–138.
- Fang, X., Wu, J., Su, S., Han, J., Wu, Y., Shi, Y., Wan, D., Sun, X., Zhang, J., Hu, J., 2012. Estimates of major anthropogenic halocarbon emissions from China based on interspecies correlations. *Atmospheric Environment*, **62**: 26–33.
- Fraser, P., Cunnold, D., Alyea, F., Weiss, R.F., Prinn, R.G., Simmonds, P., Miller, B.R., Langenfelds, R., 1996. Lifetime and emission estimates of 1,1,2-trichlorotrifluoroethane (CFC-113) from daily global background observations June 1982–June 1994. *Journal of Geophysical Research*, **101**: 12,585–12,599.
- Global Carbon Project, 2012. Carbon budget and trends 2012. www.globalcarbonproject.org/carbonbudget
- GLOBALVIEW-CH₄, 2009. Cooperative Atmospheric Data Integration Project – Methane. CD-ROM, NOAA ESRL, Boulder, Colorado. Also available on Internet via anonymous FTP to [ftp.cmdl.noaa.gov](http://ftp.cmdl.noaa.gov/products/globalview/ch4/), Path: [products/globalview/ch4/](http://ftp.cmdl.noaa.gov/products/globalview/ch4/), 2009
- GLOBALVIEW-CO₂, 2013. Global Atmospheric Data Integration Project. 2013, updated annually. Multi-laboratory compilation of synchronized and gap-filled atmospheric carbon dioxide records for the period 1979–2012 (obspack_co2_1_GLOBALVIEW-CO2_2013_v1.0.4_2013-12-23). Compiled by NOAA Global Monitoring Division: Boulder, Colorado, U.S.A. Data product accessed at <http://dx.doi.org/10.3334/OBSPACK/1002>
- Jiang, X., Ku W.L., Shia, R.-L., Li, Q., Elkins, J.W., Prinn, R.G., Yuk, L., Yung, Y.L., 2007. Seasonal cycle of N₂O: analysis of data. *Global Biogeochemical Cycles*, **21**: GB1006, 1–12.
- Lasa, J., Śliwka, I., 2001. Stability examination of the response of a GC equipped with an ECD working in a constant current mode. *Chemia Analityczna*, **46**: 421–431.
- Levin, I., Ciais, P., Lengenfelds, R., Schmidt, M., Ramonet, M., Sidorov, K., Tchepakova, N., Gloor, M., Heimann, M., Schulze, E.-D., Vygodskaya, N.N., Shibistova, O., Lloyd, J., 2002. Three years of trace gas observations over the Euro-Siberian domain derived from aircraft sampling – a concerted action. *Tellus*, **B54**: 696–712.
- Levin, I., Naegler, T., Heinz, R., Osusko, D., Cuevas, E., Engel, A., Ilmberger, J., Lengenfelds, R.L., Neiningner, B., Rohden, C., v., Steele, L.P., Weller, R., Worthy, D.E., Zimov, S.A., 2010. The global SF₆ source inferred from long-term high precision atmospheric measurements and its comparison with emission inventories. *Atmospheric Chemistry and Physics*, **10**: 2655–2662.
- Maione, M., Giostra, U., Arduini, J., Furlani, F., Graziosi, F., Vullo, E., Io, Bonasoni, P., 2013. Ten years of continuous observations of stratospheric ozone depleting gases at Monte Cimone (Italy) – comments on the effectiveness of the Montreal Protocol from a regional perspective. *Science of the Total Environment*, **445**: 155–164.
- Necki, J.M., Schmidt, M., Rozanski, K., Zimnoch, M., Korus, A., Lasa, J., Graul, R., Levin, I., 2003. Six-year record of atmospheric carbon dioxide and methane at a high-altitude mountain site in Poland. *Tellus*, **55B**: 94–104.
- Necki, J.M., Chmura, L., Zimnoch, M., Różański, K., 2013. Impact of emissions on atmospheric composition at Kasprowy Wierch based on results of carbon monoxide and carbon dioxide monitoring. *Polish Journal of Environmental Studies*, **22**: 1119–1127.
- O'Doherty, S., Cunnold, D., Sturrock, D.A., Ryall, D., Derwent, R.G., Wang, H.J., Simmonds, P., Fraser, P.J., Weiss, R.F., Salameh, P., Miller, B.R., Prinn, R.G., 2001. In-situ chloroform measurements at AGAGE atmospheric research stations from

- 1994–1998. *Journal of Geophysical Research*, **106**: 20,429–20,444.
- Prinn, R.G., Cunnold, D.M., Rasmussen, R., Simmonds, P.G., Alyea, F.N., Crawford, A., Fraser, P.J., Rosen, R., 1990.** Atmospheric emissions and trends of nitrous oxide deduced from ten years of ALE-GAGE data. *Journal of Geophysical Research*, **95**: 18,369–18,385.
- Prinn, R.G., Weiss, R.F., Fraser, P.J., Simmonds, P.G., Cunnold, D.M., Alyea, F.N., O'Doherty, S., Salameh, P., Miller, B.R., Huang, J., Wang, R.H.J., Hartley, D.E., Harth, C., Steele, L.P., Sturrock, G., Midgley, P.M., McCulloch, A., 2000.** A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *Journal of Geophysical Research*, **105**: 17,751–17,792.
- Quéré, C., Ie, Andres, R.J., Boden, T., Conway, T., Houghton, R.A., House, J.I., Marland, G., Peters, G.P., Werf, G.R., van der, Ahlström, A., Andrew, R.M., Bopp, L., Canadell, J.G., Ciais, P., Doney, S.C., Enright, C., Friedlingstein, P., Huntingford, C., Jain, A.K., Jourdain, C., Kato, E., Keeling, R., Klein Goldewijk, K., Levis, S., Levy, P., Lomas, M., Poulter, B., Raupach, M.R., Schwinger, J., Sitch, S., Stocker, B.D., Viovy, N., Zaehle, S., Zeng, N., 2013.** The global carbon budget 1959–2011. *Earth System Science Data*, **5**: 165–185.
- Reimann, S., Alister, J.M., Simmonds, P.G., Cunnold, D.M., Wang, R.H.J., Li, J., McCulloch, A., Prinn, R.G., Huang, J., Weiss, R.F., Fraser, P.J., O'Doherty, S., Grealley, B.B., Stemmler, K., Hill M., Folini, D., 2005.** Low European methyl chloroform emissions inferred from long-term atmospheric measurements. *Nature*, **433**: 506–509.
- Rosiek, J., Lasa, J., Śliwka, I., Róžański, K., 2007.** Application of GC and modulated ECD for the determination of SF₅CF₃ mixing ratios in the atmosphere. *Chemia Analityczna*, **52**: 235–242.
- Simmonds, P.G., Derwent R.G., McCulloch A., O'Doherty S., Gaudry A., 1998.** Long-term trends in concentration of halocarbons and radiatively active trace gases in Atlantic and European air masses monitored at Mace Head, Ireland from 1987–1994. *Atmospheric Environment*, **30**: 4041–4063.
- Simmonds, P.G., Cunnold, D.M., Weiss R.F., Prinn R.G., Fraser P.J., McCulloch A., Alyea F.N., O'Doherty S., 1998.** Global trends and emissions of CCl₄ from in-situ background observations from July 1978 to June 1996. *Journal of Geophysical Research*, **103**: 16,017–16,027.
- Śliwka, I., Lasa, J., 2002.** A method for improvement of precision and accuracy in concentration measurements based on external standard. *Chemia Analityczna*, **47**: 1–17.
- Śliwka, I., Lasa, J., Bielewski, J., Grombik, I., Limanówka, D., Rosiek, J., 2010.** Long-term measurements of CFCs and SF₆ concentration in air. *Polish Journal of Environmental Studies*, **19**: 811–815.
- Sturges, W.T., Wallington, T.J., Hurley, M.D., Shine, K.P., Sihra, K., Engel, A., Oram, D.E., Penkett, S.A., Mulvaney, R., Brenninkmeijer, C.A.M., 2000.** A potent greenhouse gas identified in the atmosphere: SF₅CF₃. *Science*, **289**: 611–613.
- Sturges, W.T., Oram, D.E., Laube, J.C., Reeves, C.E., Newland, M.J., Hogan, C., Martinerie, P., Witrant, E. Brenninkmeijer, C.A.M., Schuck, T.J., Fraser, P.J., 2012.** Emissions halted of the potent greenhouse gas SF₅CF₃. *Atmospheric Chemistry and Physics*, **12**: 3653–3658.
- Thoning, K.W., Tans, P.P., Komhyr, W.D., 1989.** Atmospheric carbon dioxide at Mauna Loa Observatory 2. Analysis of the NOAA GMCC data, 1974–1985. *Journal of Geophysical Research*, **94**: 8549–8565.