

Observations and
trends of surface CO
in Europe

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Carbon monoxide observations from ground stations in France and Europe and long trends in the free troposphere

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Continuous CO measurements performed at 3 high-altitude stations in France are analyzed for the first time. Data are provided by the new PAES (Pollution Atmosphérique à l'Echelle Synoptique) network since 2002 for the Puy de Dôme and 2004 for the Pic du Midi and the Donon. CO measurements of 5 another European stations have been analysed to put the PAES stations in an European perspective. The January 2002–April 2005 CO mean levels of surface stations capture the stratification revealed by climatological CO profiles from the airborne observation system MOZAIC (Measurement of OZone and water vapour by Airbus In-service Aircraft). The deviation between the free tropospheric reference MOZAIC and surface data above 2000 m is less than 10% and this deviation can be explained in term of spatial variability, as evidenced by MOPITT CO retrievals at 700 hPa. This suggests that, averaged at a seasonal time scale (4 months), surface data at stations above 2000 m are representative of background CO concentration.

This paper focuses then on trends since the 1980s–1990s. The comparison between old (1982–1983) and recent CO mixing ratio (2005) at the Pic du Midi leads to a 10% decrease, consistent with the continuous data series at Zugspitze (ZSP) from 1991 to 2004. This decrease was found to be mainly due to a negative trend of January–April mean levels. The decrease in CO sources over France and Europe appears to be responsible for that trend. The stable values of June–September mean levels suggest that the summertime oxidizing capacity of the atmosphere related to OH radicals is important enough to counterbalance any CO inputs into the troposphere. Our study shows a recent change in CO evolution since 2000 over Western Europe, with a slowed down decrease in CO concentration. Studying specifically the interactions between CO, CH₄ and OH turns out to be needed, however, to find definitive explanations to those observations.

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1 Introduction

The trace gas carbon monoxide (CO) plays an important role in tropospheric chemistry through the chemical interaction with its main sink, the hydroxyl radicals OH (Thompson, 1992) – sometimes called the “detergent” of the troposphere because of its action on many atmospheric pollutants. Consequently, tropospheric CO disturbances impact on numerous other species such as ozone (O₃) and methane (CH₄).

Coll et al. (2006) showed that CO is the third compound involved in local O₃ formation and may be responsible for 25% of total tropospheric O₃ production. As one of the most important O₃ precursors, CO was identified in IPCC (2001) as an important indirect greenhouse gas although it itself absorbs only little infrared radiation from the Earth.

Tropospheric CO disturbances may also affect methane concentrations (Daniel and Solomon, 1998). It has been noted that the tropospheric CH₄-CO-OH system is highly coupled (Prather, 1994). The most difficult problem in atmospheric chemistry is to evaluate the effects of a single action (for example the emission of one gas at a given location) while taking into account all the chemical processes and associated feedbacks. That is why the long-term trends of CH₄, CO and OH are often studied together thanks to global chemistry models (Zhang et al., 2001; Kanakidou and Crutzen, 1999; Wang and Prinn, 1999).

The analysis of CO evolution in the lower troposphere is thus of primary interest. The first CO observations were performed in the 1970s and revealed increasing CO mixing ratios at the north-hemispheric scale. CO measurements in ice cores have indicated that the CO concentration was about 50–90 ppb during the pre-industrial period. Current results of Assonov et al. (2007) showed that CO in the Southern Hemisphere has increased by about 38 % during the last 100 years. Haan and Raymund (1998) found a positive trend of 0.35 ppb/yr between the 1920s and the 1950s from analyses of air bubbles trapped in Greenland ice cores. Observations at different places in the Northern Hemisphere revealed growing CO concentrations at the hemispheric scale between the early 1950s and early 1980s, with a rate of 1–2 ppb/yr (Zander et al., 1989; Yurganov

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et al., 1999). From the 1980s, Khalil and Rasmussen (1994) showed a positive trend of about 1 ppb/yr up to 1988 and then a reversed trend of -2.6 ppb/yr from 1988 to 1992. This decrease during the late 1980s and early 1990s was also noticed by Novelli et al. (1994) who found a decrease between 1991 and 1993 of 5.9 ppb/yr. Measurements since 1995 showed a continuous global decrease of CO mixing ratios but at a significantly reduced rate (Novelli et al., 2003; Mészáros et al., 2005). At present time, concentrations could reach around 1–10 ppm in urban areas and about 150 ppb in clean areas far away from local sources of pollution in mid-latitudes of the Northern Hemisphere. Novelli et al. (2003) and Mészáros et al. (2005) depict an overall long-term negative trend in tropospheric CO in the Northern Hemisphere during the 1990s, perturbed by short periods of increase induced by important biomass burning events.

Nowadays, more than half of the CO emissions has an anthropogenic origin, attributable to incomplete combustion of fossil hydrocarbons for transport, industrial processes (both relatively constant along the year) and heating (with a peak during winter) or biomass burning. About 45% of CO sources has a photo-chemical origin: 400–1000 Tg CO/yr are produced during the oxidation of methane; between 200–600 Tg CO/yr are released during natural and anthropogenic non-methane hydrocarbons (NMHC) oxidation, particularly during spring (IPCC, 2001).

Most of the significant CO sources and sinks have been identified but there are still large uncertainties in the CO budget. Fire emissions can perturb CO concentrations at regional and global scales, disturbing oxidation/reduction chemistry in the troposphere (Edwards et al., 2004). Novelli et al. (2003) showed that enhancement of tropospheric CO in 1997 and 1998 resulted from exceptionally widespread wildfires which provided a strong pulse of CO to the atmosphere. Modification in distribution of sources and sinks or increasing of OH concentrations in the atmosphere could both explain such a decrease in CO concentrations, but so far, the causes of declining CO concentrations are not well established. Several studies have also investigated the possible causes for the decrease of atmospheric CO at the beginning of the 1990s:

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- [Bakwin et al. \(1994\)](#) and [Granier et al. \(1996\)](#) proposed a significant anthropogenic emission decrease at European scale and a particularly sharp decrease of CO emission from ground transport.
- [Gleason et al. \(1993\)](#) attributed that decrease to the eruption of Mt. Pinatubo in June 1991 and the consecutive severe atmospheric perturbations: one of them is the decrease in the stratospheric ozone concentrations (less stratospheric ozone leads to more tropospheric OH and consequently to a decrease of tropospheric CO concentration). No consensus currently however exists about the evolution of OH concentrations in the troposphere. [Dlugokencky et al. \(1998\)](#) suggest that global OH concentrations were essentially constant between 1984 and 1997; [Karlsdottir and Isaksen \(2000\)](#) argue for a global OH increase by 0.5% over the last two decades. The recent study by [Prinn et al., \(2005\)](#) showed that OH concentrations in 2003 were approximately the same as in 1979.
- [Zhang et al. \(2001\)](#) used a global two-dimensional chemistry model to investigate the links between CO, CH₄ and OH in the sudden decrease in CO in the beginning of the 1990s at the global scale. They evaluated that the depletion of stratospheric ozone accounts for 30% and the decrease of CO emissions for about 70% in the CO concentrations decrease in the beginning of the 1990s. Moreover, [Zhang and Wang \(1999\)](#) showed that the decrease of CO emissions could significantly counteract the growth of methane in the 1990s (see Fig. 1).

To summarize, long term surface CO records can deliver essential information on CO changes in the lower troposphere, and consequently on CH₄ or ozone concentration changes. The evolution of CO is not regulated by the European protocols of Göteborg or Geneva aiming to improve the air quality in Europe for the year 2010. However, these protocols concern Volatil Organic Compounds (VOCs). Thus, it indirectly affects the CO emissions as anthropogenic VOCs and CO have common sources. Is the evolution of tropospheric CO over Europe since the 1980s, at least partly, a consequence of European protocols? As a contribution to answer this question, calculations of long

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term trends in CO over Western Europe are analyzed in the present paper, and a discussion on the balance between emissions, sources and sinks, is proposed.

The originality of our approach lies on different aspects:

– First we investigate the question of the spatial and temporal representativity of surface station with respect to free tropospheric conditions. This paper is, to our knowledge, the first one where surface data are compared with both airborne and spaceborne measurements. The MOZAIC (Measurement of OZone and water vapour by Alrbus in-service airCRAFT, [Marenco et al., 1998](#)) CO profiles sampled above Frankfurt since 2002 allowed the investigation of the stratification of CO concentration under true free-tropospheric conditions (measurements unaffected by surface effects). Since the CO distribution in the troposphere is dependent on the variability and distribution of CO sources, and on the atmospheric transport at different scales, the spatial CO distribution is heterogeneous, and space-borne remote sensing is needed to capture it. Indeed, [DeMazière et al. \(2004\)](#) and [Novelli et al. \(1998\)](#) showed that it is very difficult to document the spatial distribution of CO with in-situ measurements, because this would imply to analyze a dense network of stations. The Measurement of Pollutants in the Troposphere (MOPITT) instrument on the Terra satellite provides CO concentration maps over Europe since 2000. The three datasets will be compared in terms of trends and seasonal variations.

– Tropospheric CO measurements have only become systematical at high-altitude sites in Europe from the 1990s (1991 for Zugspitze or 1996 for Jungfrauoch). Such measurements were not systematical over France before 2004, when the network PAES was brought into service. However, a pioneer series of CO measurements was collected from 1981 to 1983 at Pic du Midi (2877 m a.s.l., Pyrenees, a station of the PAES network). This series has not yet been exploited. The observation network PAES provides CO measurements at 3 high-altitude sites over France since 2004. This paper provides an opportunity to analyze CO trend in the context of decreasing emissions, on the basis of data from this recent network. The present study also includes four well studied stations of the World Data Center for Greenhouse Gases (WDCGG) network

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in Western Europe, for which continuous data since the early 1990s are available.

The networks and datasets are described in Sect. 2. The spatial and temporal representativity of the surface stations is analysed in Sect. 3 according to the MOZAIC and MOPITT data. In Sect. 4, trends are discussed in relation of varying sources and
5 sinks.

2 Description of the observation networks and datasets

2.1 Surface data

The French network PAES (PAES: French acronym for atmospheric pollution at synoptic scale, see <http://paes.aero.obs-mip.fr/paes.html>) is devoted to the long-term obser-
10 vation of synoptic scale photo-oxidant pollution. It provides measurements of ozone and of some of its precursors such as nitrogen oxides (NO_x) and CO from stations away from any major source of pollution. In the same way, the WDCGG (see <http://gaw.kishou.go.jp/wdcgg.html>) was established in October 1990 to collect and distribute data on greenhouse and related gas concentrations among them carbon dioxide
15 (CO_2), methane (CH_4), ozone (O_3), carbon monoxide (CO) and Volatile Organic Compounds (VOCs).

The sites are displayed in Fig. 2 and details are given in Table 1. The site elevations range from 755 to 3580 m and cover well the low troposphere. PAES provides continuous CO measurements from three stations in France located in the main mountainous
20 areas. The Pic du Midi, an isolated summit in the Pyrenees, is located 150 km to the east of the Atlantic coast and directly exposed to dominant oceanic westerlies. The Puy de Dôme is also an isolated summit in the Massif Central. The Donon tower in the Vosges emerges from a dense forest. CO measurements are available since June 2002 for PDD and since June 2004 for PDM and DON. Previous measurements made
25 in 1982 and 1983 at PDM are also analyzed in this study.

Recent CO data (2002–2006) from the 3 French stations were collected at a various

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sampling rate (5 or 15 min) using a 48CTL Thermo Environment gas filter correlation CO analyzer, improved to enable low CO concentration measurements (Nédélec et al., 2003). Achieved performances are of the order of ± 5 ppb ($\pm 5\%$) of precision for a 30 s response time (instead of 20 ppb (10 %) for the original CO analyzer). A coherent and synchronized dataset has then been obtained by averaging data from stations on a hourly basis. A monthly averaged dataset derived from the latter is also used in this study.

Previous measurements during the 1980s at PDM have been performed with gas chromatography with FID (Flame Ionization Detector), described by Marengo et al. (1989). The precision of the chromatographical measurements above 10 ppb is about 0.5% (1 ppb) and the estimated accuracy is 1% (2 ppb).

Moreover, hourly and monthly data at Hohenpeissenberg (Alps, Germany, 985 m), Schauinsland (Black Forest, Germany, 1205 m), Zugspitze (Alps, Austria, 2960 m) and Jungfraujoch (Alps, Switzerland, 3580 m) provided by the WDCGG complement the study. The station Hohenpeissenberg (HOH) is described by Naja et al. (2003); more details about the research station Jungfraujoch (JUN) are given by Brönnimann et al. (2000) and Schuepbach et al. (2001).

2.2 MOZAIC data

The MOZAIC program (<http://www.aero.obs-mip.fr/mozaic/>) was initiated in 1993 by European scientists, the aircraft manufacturer Airbus Industry and airlines carrier companies (Air France, Lufthansa, Sabena and Austrian Airlines) to collect experimental data. MOZAIC consists of automatic and regular measurements of ozone, carbon monoxide, nitrogen oxides and water vapour by five long range passenger airliners A340 flying all over the world. Measurements are performed with a sampling rate of 4 s, corresponding to a 50–100 m resolution in the vertical profiles sampled during the ascent/descent phases of the aircraft. MOZAIC data provide, in particular, detailed ozone and water vapour climatologies in the troposphere and lowermost stratosphere since 1994 as well as CO and NO_y since 2001. Details on the measurements per-

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formed by the MOZAIC program can be found in [Marengo et al. \(1998\)](#); [Thouret et al. \(1998\)](#); [Nédélec et al. \(2003\)](#). CO measurements during MOZAIC ascent and descent vertical profiles over Frankfurt (113 m, 50.03° N, 8.57° E) for the period January 2002–April 2005 were used. Data in May, June, September and December 2002 are missing. The MOZAIC dataset is complete in 2003 and 2004. Data are available until April 2005. The CO analyzers are similar to those of the PAES stations (see Sect. 2.1).

2.3 MOPITT data

The TERRA/MOPITT instrument ([Drummond and Mand, 1996](#)) has been monitoring global tropospheric CO from March 2000 until now. These data have been intensively validated ([Emmons et al., 2004, 2006](#)). The pixel size is 22 km×22 km and the vertical profiles are retrieved on 7 pressure levels (surface, 850, 700, 500, 350, 250 and 150 hPa). The maximum likelihood method used to retrieve the MOPITT CO, is a statistical combination of the measurements and a priori information ([Rodgers, 2000](#)). The retrieval profiles are characterized by their averaging kernels which give information on the vertical resolution of the measurements. In particular, the Degree of Freedom for Signal (DFS), which is the trace of the averaging kernel matrix, indicates the number of independent pieces of information contained in the measurements. It depends, via the surface temperature, on the latitude and the alternating day/night. Furthermore, in this study, we only consider daytime MOPITT CO (Version 3) retrievals at 700 hPa with less than 40% a priori contamination to insure a consistent dataset of good quality.

Over Europe, the estimated retrieval error for the CO mixing ratio is about 20 ppb (20%) at 700 hPa ([Pfister et al., 2004](#)). Validation of the MOPITT data have been performed by comparisons with in-situ measurements from aircraft ([Emmons et al., 2004; Deeter et al., 2004](#)). The MOPITT data validation ([Emmons et al., 2004, 2006](#)) using aircraft in situ CO profiles indicates an average bias over all validation sites of 4.4 ± 12 ppb (5 ± 12 %) at 700 hPa.

In this study, we directly compare the MOPITT retrievals above the measurement sites, to in-situ data. To this goal, MOPITT data were retrieved at 700 hPa at the location

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of the three stations around 3000 m. a.s.l. (JUN, ZSP and PDM). Two datasets have been produced, averaging the MOPITT data in a circle centered on the station and with radii of 300 and 500 km (below 300 km, too few points are available from MOPITT to have statistically pertinent dataset). Note that a rigorous comparison would imply to apply the averaged kernels representative of the MOPITT CO to a “true” profile representative of the troposphere. Hence, an important caution has to be expressed here: the proposed comparison is indicative and in no case should be considered with the view to assess the quality of the MOPITT retrievals.

An other MOPITT dataset has been realized, centered on the 45° N, 4.5° E, with a radius of 1500 km in order to take into account all the stations and the Frankfurt airport, and provide a value expected to be representative of Western Europe.

3 Spatial and temporal representativity of surface station

Since CO sources are mainly anthropogenic and/or come from biomass burning, the mean CO concentration decreases with altitude in the first kilometres of the lower troposphere (Fischer et al., 2006). Surface data have consequently to be compared to airborne and spaceborne data at similar altitudes.

A particular attention can be paid to the three highest stations around 3000 m (PDM, ZSP and JUN). Due to their high altitude, they are expected to be the most representative of the background conditions and large scale transport. They are indeed supposed to be little influenced by nearby emissions sources and their altitude is close to the level 700 hPa. That is why surface time series of JUN, ZSP and PDM can be compared to MOPITT 700 hPa retrieval, unlike the other stations that are too low to give sense to a comparison.

The Fig. 3 proposes a comparison over the January 2002–April 2005 period of the mean CO levels as a function of altitude between:

- the set of surface stations vertically ranged in the first 4 km of the troposphere,
- a climatology of MOZAIC vertical profiles above Frankfurt,

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– CO mean values provided by an average of 700 hPa MOPITT data over an area of 300 km around each of the three highest stations (PDM, ZSP and JUN).

Monthly averages from the three datasets are available for at least 80% of the considered period. Details on missing data are given in the next three paragraphs.

5 The mean CO levels and associated standard deviation from the PAES and WD-CGG stations over the 41-month period were calculated from the hourly datasets (see Sect. 2.1). However, PDM and DON have been excluded from Fig. 3 because missing data exceed 50%. The data coverage for the other stations is better than 90%.

10 For this period, the available profiles above Frankfurt amount to 2652, which correspond either to ascent or descent from/to the Frankfurt airport. Too few profiles are available for 4 individual months out of the 41-month period, so that these months have not been considered. The MOZAIC flights are not uniformly distributed over the 12 months of a year. There are indeed about 25% more MOZAIC flights in summer than in winter. In addition the frequency of MOZAIC flights is globally increasing from 2002 to 2005. In order to obtain a profile representative of the annual mean CO profile over Frankfurt for this period, and to avoid overweighting the summer period, the available MOZAIC profiles were reduced to monthly mean profiles with corresponding standard deviation. The data were gridded on the vertical on a regular 50-m mesh, in asl coordinate. Thus we obtained 37 monthly mean profiles over Frankfurt airport. The final
20 mean MOZAIC profile (displayed in Fig. 3) was produced by averaging together the 37 monthly mean profiles. The variability interval also results from averaging the 37 monthly standard deviations.

25 The MOPITT values around the three highest stations were obtained by averaging the 41 monthly mean and 41 corresponding monthly standard deviation over the January 2002–April 2005 period following the same process as for MOZAIC. The satellite provides one measurement every 3 days only under clear sky conditions. Therefore, the mean monthly MOPITT values does not involve a constant number of pixels. The Table 2 provides the maximum (which occurs in summer period), the minimum (which occurs in winter period) and the mean pixel number to form the monthly means.

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Figure 3, and especially the mean MOZAIC profile, shows that the CO mixing ratios rapidly decreases in the first few hundred metres down to 120 ppb above 2000 m. A rather good agreement exists between MOZAIC and surface data in the altitude range 700–3500 m. The mean relative deviation between the MOZAIC and surface data is less than 8% all along the vertical. Since MOZAIC data are not influenced by surface and local effects above 1200 m. a.s.l. (Chevalier et al., 2007), the surface data can be considered as representative of free-tropospheric conditions. Note also the reasonable agreement of MOPITT data with the two other datasets. The MOPITT mean values remains unchanged when a larger radius around the stations (500 km instead of 300 km) is considered (not shown). Note that a specific urban influence above Frankfurt might play a role in the very low levels. According to the comparison between ozone surface data and MOZAIC profiles made in Chevalier et al. (2007), the ozone profile is marked by a transition in ozone level and variability around 1200 m. Such a transition does not seem to exist for CO.

The CO monthly variations of the 7 European stations are displayed in Fig. 4 from mid 2003 until mid 2005 (note that 2004 is the only year covered simultaneously by all the stations during more than 7 months). The CO seasonal maximum occurs in March or April and the minimum between June and September. This CO seasonal cycle may be interpreted considering its varying sources and sinks (Yurganov et al., 1999). In summer, the maximum solar radiation causes increased OH concentration and in turn decreased CO concentration in troposphere. In fall, CO mixing ratios begin to increase, due to weaker solar radiation. Transport or industrial processes are rather constant throughout the year but, in winter, these CO emissions are not compensated by the OH sink. Thus, reduced OH concentrations at mid- and high-latitudes due to less solar radiation allow an accumulation of CO in the troposphere in winter. Heating is a major additional anthropogenic CO source. In spring, CO mixing ratio begins to drop, due to increasing solar radiation. However, the role of biogenic non-methane hydrocarbons (NMHCs) emissions has also to be considered because the seasonal variations in NMHCs emissions are considerable throughout the year (Guenther et al.,

1995). The NMHCs oxidation is an important source of CO at global scale which can contribute significantly to a CO production during late spring, probably important enough to partly counteract its destruction by increasing OH in the troposphere.

Seasonal variations at the different stations (not presented here) have been analyzed over a longer period, between 1991 and 2005: minima and maxima occur on varying dates according to the year for a given station. CO minima occur from June to September (JJAS) whereas CO maxima occur from January to April (JFMA). The CO seasonal cycle (high values during late winter – early spring and low values in summer) is coherent with observations reported in the literature (Khalil and Rasmussen, 1984; Marengo, 1986; Dianov-Klokov and Yurganov, 1989; Zander et al., 1989; Novelli et al., 1992; Pougatchev and Rinsland, 1995; Jaffe et al., 1998; Narita et al., 1999). The inter-annual variations are probably linked to varying synoptic conditions (temperature, solar exposure) from year to year at the different places.

Figure 5 represents CO on the vertical as in Fig. 3, but for the JJAS (2003+2004) and JFMA (2004+2005) periods. Despite the distinction between the two extreme seasons for CO (JFMA and JJAS), a good agreement still exists between the three datasets. The mean relative deviation between the MOZAIC and surface data is now less than 6% at all vertical levels during the JFMA period. During the JJAS period, it is less than 10% for the stations above 2000 m but more than 10% for stations below. This clearly shows the influence of the boundary layer on the surface station measurements during the JJAS period. This result is consistent with the conclusions of Chevalier et al. (2007) regarding ozone in summer.

Figure 6 shows the spatial variations of CO concentrations at 700 hPa from MOPITT over Europe on average over the JJAS (2003+2004) and JFMA (2004+2005) periods. Features of the spatial variability at the scale of few hundred kilometers are captured in those maps. The surface data well captures the positive CO gradient existing between PDM, JUN and ZSP both in JFMA and JJAS. MOPITT indicates relative differences of the order of 10% between the sites. Therefore, the spatial variability could explain most of the deviation between station mean values and the MOZAIC reference, found

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in Fig. 3 and 5.

The amplitude of the seasonal cycle (Figs. 7) also depends on altitude. The amplitude calculation is based on the difference between JFMA (2004+2005) and JJAS (2003+2004) means (DON and PDM have to be interpreted more caustiously because monthly data are available only in JJAS 2004 and JFMA 2005). The figure reveals a clear transition around 1000 m. Above, the seasonal amplitude is rather constant in relative value (of about 0.2). This is an indication that the CO background concentration is mostly modulated by chemical destruction efficiency (linked to OH availability), since the destruction rate is proportional to the CO concentration. Below, the varying amplitude is about twice. This might be attributed to seasonally varying emissions (e.g. heating in winter) but more likely also to enhanced vertical exchanges in the boundary layer in summer and hence enhanced venting of the surface emissions (Beekmann et al., 1997; Colette et al., 2005; Colette and Ancellet, 2005).

To conclude, the low deviation between free-tropospheric measurements provided by MOZAIC and the surface data (below 10% when surface data are averaged over more than 8 months, for all stations above 2000 m and whatever the season) shows that in averages over a seasonal time-scale (about 4 months), local effects are sufficiently smoothed so that surface stations above 2000 m may be considered as reasonably representative of tropospheric conditions for CO measurements. It is also true for the lowest stations if the JFMA period only is considered.

The representativity of surface station has also been estimated at the monthly scale. Time series of monthly averaged surface data have been compared with those provided by MOZAIC and MOPITT (300 km around each stations) from December 2001 up to July 2005 (Fig. 8). The variations of the different time-series are quite similar, showing not only the seasonal cycle but also some features of the interannual variability (e.g. lower CO levels in summer 2004 than in summer 2002 and 2003). The relative difference between surface data and MOZAIC data is given in Fig. 9. The deviation is now higher than when considering seasonal means. During the JFMA period, the deviation is in general below 30% for all the stations. During the JJAS period, it is also

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below 30% except for stations below 1200 m where the deviation exceeds 40%. In summer, local effects (e.g., slope breezes, mixed boundary layer) can explain such a large deviation from the tropospheric reference.

To summarize, the comparison between surface, MOZAIC and MOPITT time series show that if, generally speaking, the seasonal cycle of CO measurement from different instrument is correlated, however, on short period (one month or less), some local effects may affect concentrations at different location and measurements at surface station are poorly representative of background free-tropospheric conditions (with quite large uncertainty of 30%). Averaged on 4 months and more, however, the deviation between free-tropospheric reference MOZAIC and surface data drops below 8%, for all the station in the JFMA period and for the 3 highest during the JJAS period. Further, this deviation can be attributed to the spatial variability that has been evidenced with the MOPITT seasonal maps. PDM in particular is quite far from Frankfurt and MOPITT shows a clear positive gradient in between. This explains why mean CO values there are systematically found lower than the MOZAIC reference in Frankfurt. The surface station would probably agree much better with a tropospheric reference (airborne or balloon measurements) taken in a radius of 300 km around the station. The next part will deal with trends at the three highest stations, established on annual and seasonal mean concentrations.

4 CO trends over western Europe since the 1980s and link to source decrease

4.1 Observations at ZSP and PDM

The trend for 1991—2004 calculated from annual mean CO levels at ZSP is found to be -0.84 ± 0.95 ppb/yr (Fig. 10, ZSP). The given uncertainty corresponds to a 90% confidence interval. The inter-annual variability was estimated as the square-rooted quadratic mean deviation of the annual mean CO concentrations from the trend curve. The found value is 7.46 ppb. Hence, at a rate of -0.84 ppb/yr, 9 years are needed for

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CO trends to emerge from the inter-annual noise.

In Sect. 3, we showed that the maximum seasonal concentrations could occur between January and April, and the minimum between June and September. Figure 10 (ZSP) also presents trends for these two seasons (JFMA and JJAS, respectively).

For the JFMA season at the ZSP station, a negative trend of -1.49 ± 1.50 ppb/yr was found whereas no trend is evident during the JJAS season due to a large uncertainty (-0.28 ± 1.36 ppb/yr). This shows that the negative trend on yearly means is due to decreasing CO values in winter

Trends at ZSP have also been calculated on running decades starting in 1991, 1992, 1993, 1994 and 1995 (Table 3). If over the longest period (1991–2004), trends are significant and negative (as well as for the two decades 1991–2000 and 1992–2001), a closer look at the decadal trends and their evolution in time shows a decrease of both rate and statistical significance, and an increase of the inter-annual variability.

At PDM (Fig. 10 PDM), no continuous data series is available on the long term but a past short series nevertheless exists. CO levels in 1982 and 1983 can be compared to recent ones (2005). CO mixing ratios were 133.8 ppb in 1983 (132.6 ppb in 1982 but with missing data in August) and are nowadays of 117.2 ppb (2005). Over the 23-year period (that is much larger than the estimated 9 years at ZSP needed for a significant trend to emerge from the interannual noise), a decrease of 13 ppb is found (this value is also well above the interannual variability estimated at ZSP). This correspond to -0.71 ppb/yr (-10%) over the last two decades. No confidence interval can be reasonably discussed here due to the small number of data points used for the trend calculation. However, both the time interval and the amplitude of the CO decrease allow the definitive conclusion of a negative trend at PDM.

Note that the analytical technics used were different in 1982–1983 and 2005. An inter-comparison between these two analytical methods at PDM was made. The Fig. 11 presents between July and December 2004 the comparison between ponctual measurements (bottle sampling then gas chromatography in laboratory) performed weekly by the RAMCES organization (Réseau Atmosphérique de Mesure des

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Composés à Effet de Serre, see <http://www.ipsl.jussieu.fr/services/Observations/fr/RAMCES.htm>), and the continuous measurements by infrared CO analyzer (PAES). PAES CO data were averaged within one hour around the RAMCES measurement time and corresponding standard deviation were calculated. The calculated relative error between RAMCES and PAES data is about 6.4%. The regression line slope is 1.0 ± 0.2 , which means that the comparison is satisfactory. The intercept is about 7.5 ± 15 , showing that PAES measurements are in average 7.5 ppb higher than RAMCES measurements. Even if the relative error between chromatographical and IR-analyzer measurements is applied, and the bias taken into account (i.e. PAES (2005) – $7.5 \text{ ppb} \pm 15 \text{ ppb}$), the trends observed at the PDM station remains negative since the 1980s, between -0.4 and -1.7 ppb/yr . So, despite uncertainty on a quantitative estimation of the CO trend at PDM, it can be concluded that the mean CO level in 2005 is significantly lower than in 1982–1983.

To summarize, a negative trend between the early 1980s and 2005 was found at PDM with an order of magnitude of -1 ppb/yr . A negative trend has also been found for the 1991–2004 period at ZSP at a rate of $-0.84 \pm 0.95 \text{ ppb/yr}$. No meaningful trend has been found out for the summer (June–September) period at ZSP. Trends during the January–April period are responsible for the global decrease of annual mean CO concentration. This result suggests that during the JJAS period, when the oxidizing capacity of the atmosphere is maximum, OH radicals are abundant enough to absorb any variations in CO input into the atmosphere. During the JFMA period, on the contrary, there are not enough OH in the atmosphere to balance enhanced emissions (heating in winter and non-methanic hydrocarbons in spring). The causes of the decrease in CO concentrations since the 1980s hence has to be searched in late winter – early spring. Furthermore, if a global decrease is observed on the 1980–2005 period, it seems that on the last decade, the decrease has slowed down. This is consistent with trends established from MOPITT data, averaged over an area centered at (45° N , 4.5° E), with a radius of 1500 km in order to cover all the studied stations (Fig. 12). It appears that since 2000, the CO concentration trend is positive (although not statistically significant).

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4.2 Role of anthropogenic emissions on CO concentration evolution

Recent modelling studies (Zhang and Wang, 1999; Zhang et al., 2001) seem to show that the decrease in CO emissions is mainly responsible for CO concentration decrease (70%) and could also explain the slope break in CH₄ evolution in the 1990s (Fig. 1, period II). The observed fast changes in atmospheric CO suggests a change in the balance between the sources and sinks, in which anthropogenic emissions cloud play a key role to explain decreasing CO concentrations in the lower troposphere.

Novelli et al. (2001) showed that the summertime averaged CO concentrations north of 30° N were correlated with area burnt by forest fires in North America and Russia: 14% of the CO variability in the extra-tropical Northern Hemisphere could be explained by boreal forest area burnt in North America, 53% by burnt area in Russia and 63% by the combination of both. However, biomass fires are not frequent during the January–April period. Data of total number of fire pixels have been obtained from the European Space Agency website (<http://dup.esrin.esa.int/ionia/wfa/index.asp>) from 1997 to 2005. It appears no evident correlation in Fig. 13 between the yearly total number of fire pixels over Europe, North America and Asia, and CO concentrations from a subset of European surface stations (for which data are available between 1997 and 2005). Moreover, Mészáros et al., 2004 showed that the total incremental change in CO concentrations by the European sources is twice as important as the inward advection (transport from other continents).

At a national scale, Fig. 14 represents anthropogenic CO sources in France since the 1960s provided by the CITEPA (Centre Interprofessionnel Technique d'Etudes de la Pollution Atmosphérique, see <http://www.citepa.org>). The significant decrease of anthropogenic CO sources from 1973 (corresponding to the first oil crisis which induced French policies to reduce energy consumption) to 2004 is attributable to improved combustion efficiency in transport (cyan) and in industrial processes (green). It can be estimated that CO emissions decreased by 62% and 44% in 2004 compared to the reference year 1980 and 1990, respectively.

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This decrease in CO emissions was also evidenced at the European scale. [Mészáros et al. \(2005\)](#) showed that the primary anthropogenic emissions from fossil fuel combustion and industrial processes in Europe decrease at a fairly constant annual rate of about 4%/yr between 1995 and 2000, while the secondary anthropogenic CO source strength was reduced at a rate of about 3%/yr. [Vestreng et al. \(2004\)](#); [Derwent et al. \(2003\)](#) established that CO emissions have been reduced by 45% in Europe since the late 1980s. [Karlsdottir et al. \(2000\)](#) showed by means of a 3-D global chemistry tropospheric model that simulated CO concentrations in the boundary layer decreased by -1.94 ± 0.42 ppb/yr in Eastern Europe over the period 1980–1996, which is consistent with the decrease observed at PDM for the same period. They also show that changes in CO concentrations are related to a large extent by changes in surface emissions, above all in the Northern Hemisphere.

The negative trend in CO was slowing down along running decades from 1991–2000 to 1995–2004 (Table 3). A comparable evolution of CO emission decrease in France is shown in Table 4. Further (even if no significant trends can be established over a 5-year period) Fig. 12 (MOPITT) as well as the annual mean CO levels at ZSP suggest a slight increase of CO since 2000. Figure 14 also shows a simultaneous stabilization of CO emissions (or at least a slower decrease, of only 10% between 2000 and 2004).

To conclude, clear indications are provided here that the decrease of emissions during the 1990s in Europe impacted on the CO concentration. The 1991–2004 decrease in CO concentration can thus appear to be a consequence of the European policy of controlled anthropogenic emission and the global efforts made to reduce the CO emissions at the European scale.

The decrease in CO concentration (consecutive to decrease in CO emissions) might also explain, at least partly, the stabilization in CH₄ concentration that has stopped growing since the 2000s (period III in Fig. 1). Less CO in the atmosphere indeed leaves more OH radicals available in the troposphere to oxidize CH₄. However, the decrease in CH₄ emissions (CITEPA/CORALIE/format SECTEN (update from the 23 of February 2006) available on <http://www.citepa.org>) can also contribute to this recent evolution.

5 Conclusions

The present study is a first analysis of continuous CO measurements at 3 French high-altitude stations of the PAES network. It complements a similar study concerning ozone (Chevalier et al., 2007). Those stations cover an altitude range between 755 m and 2877 m. Four other mountainous stations located in Germany, Switzerland and Austria are also included in this study in order to put the PAES measurements in an European context. The period commonly covered by all station measurements goes from January 2002 until April 2005.

The surface observations have been compared to a climatology of CO vertical profiles provided over Frankfurt by MOZAIC aircraft, and to MOPITT data over western Europe. This comparison provides an overall agreement better than 10% and shows that seasonal means of CO concentrations at high-altitude (around 2000 m) surface stations are representative of background tropospheric CO. Most of the difference can be explained by the spatial variability revealed by MOPITT charts at 700 hPa over Europe. For that reason, seasonal spaceborne mapping of CO in the low troposphere is a great help to analyse CO surface data.

A good qualitative and quantitative agreement for the seasonal cycle was found between the 3 databases, with CO minimum values between June and September (JJAS) and CO maximum values between January and April (JFMA). Also features of the interannual variability are commonly captured by the three datasets.

In addition, previous measurements (1982–1983) have been compared to recent data (2005) at the PDM station, showing a 10% global decrease of mean CO concentrations in two decades. The trend observed at the PDM station is consistent with that calculated at ZSP station from a continuous data series from 1991 to 2004. A more detailed analysis shows that this trend on annual mean values is mainly due to the negative trend of mean values over the January–April period. Conversely, no trend is found for summer mean values. This result suggests that during June–September period, the oxidizing capacity of the atmosphere via OH is important enough to counterbalance any

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major CO perturbations in the troposphere. For the January–April period, the decrease of CO sources in France and Europe appears to be the main reason explaining the CO concentration decrease in the lower troposphere. This decrease in CO is coherent with the slowed down increase of methane in the last decade, according to other studies (e.g. Zhang and Wang, 1999). However, this link still needs to be demonstrated.

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Table 1. Characteristics of the measurement sites used in this study. * IMK-IFU: Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Germany.

Site	Abbrev.	Altitude (m)	Coordinate	Description	Organisation	Start	End
Donon	DON	755	48°30 N,7°08 E	Vosges Mountains	PAES	June 2004	May 2006
Hohenpeissenberg	HOH	985	47°48 N,11°01 E	Pre-Alps	WDCGG	Jan. 1995	July 2005
Schauinsland	SCH	1205	43°02 N,7°55 E	Black Forest	WDCGG	Aug. 2001	July 2005
Puy de Dôme	PDD	1465	45°46 N,2°57 E	Massif Central	PAES	April 2004	Nov. 2005
Pic du Midi	PDM	2877	42°55 N,0°05 E	Pyrenees	PAES	June 2004	May 2006
Zugspitze	ZSP	2960	47°25 N,10°59 E	Alps	WDCGG/IMK-IFU*	Jan. 1991	Dec. 2004
Jungfrauoch	JUN	3580	46°33 N,7°59 E	Alps	WDCGG	April 1996	Dec. 2005

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Table 2. Averaged pixel number to obtain CO monthly mean values from MOPITT in a radius of 300 km around PDM, ZSP and JUN.

	Max	Min	Mean
PDM	2257	53	671
ZSP	1562	2	479
JUN	2003	2	498

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Table 3. Trends and corresponding 90% confidence intervals (in ppb), inter-annual variability (I.V. in ppb) and decrease percentage (%) of annual CO means over the indicated decades at ZSP.

ZSP	1991–2000	1992–2001	1993–2002	1994–2003	1995–2004	1991–2004
Trend	-1.61 ± 1.51	-1.97 ± 1.59	-1.35 ± 1.8	-0.94 ± 1.95	-0.29 ± 1.89	-0.84 ± 0.95
I.V	5.59	5.86	6.64	7.20	6.99	7.46
%	10.1	12.3	8.7	6.1	2.0	7.7

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CO emissions	1991–2000	1992–2001	1993–2002	1994–2003	1995–2004	1991–2004
%	34.7	35.2	35.3	34.9	33.8	36.8

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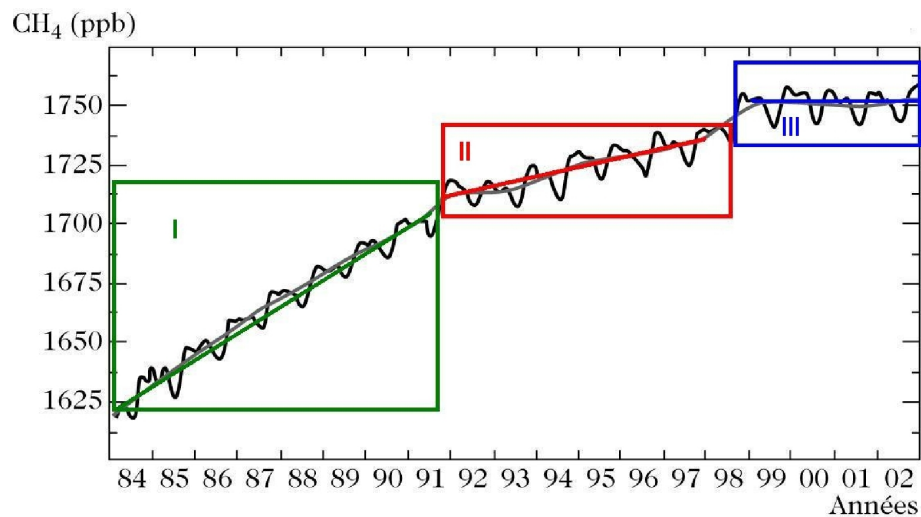


Fig. 1. Evolution of global CH₄ concentrations since the 1980s. Courtesy of [Delmas et al. \(2005\)](#).

HORIZONTAL SECTION NINF= 2 NISUP=201 NJINF= 2 NJSUP=121

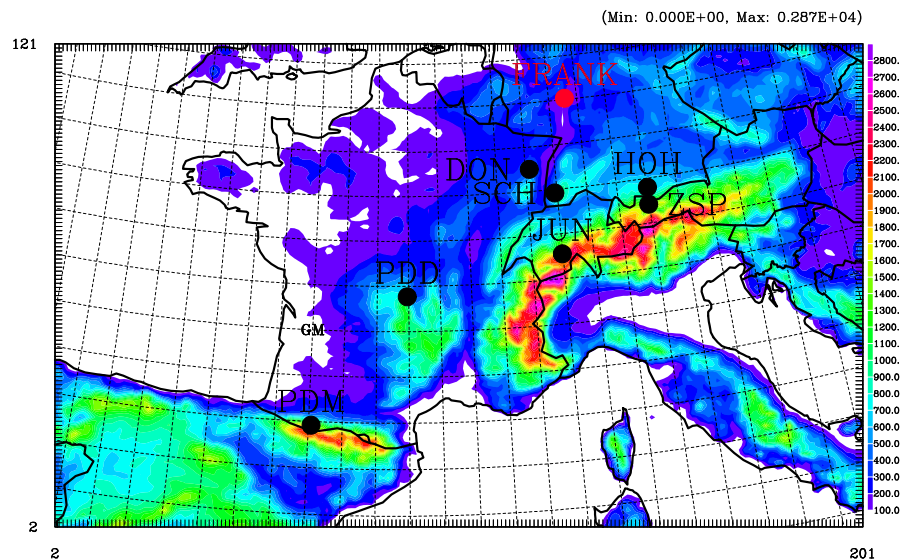
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PGD FRA-AUT 10km.dia.Z

Fig. 2. Locations of the monitoring sites used in this study. See station full names and characteristics in Table 1. (The colorscale represents terrain elevation, in m.)

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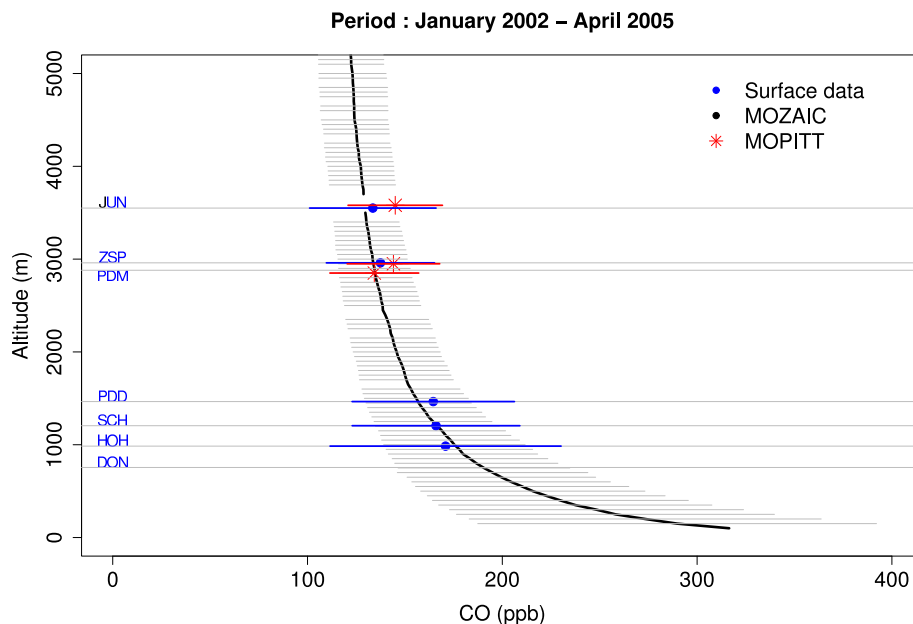


Fig. 3. Comparison between MOZAIC profiles above Frankfurt (black and grey), surface stations data (blue) and 700 hPa MOPITT CO around JUN, ZSP and PDM (red). Bold line and dots: January 2002–April 2005 mean CO level; bars: ± 1 standard deviation, see text for details on the calculation). Covered period: January 2002–April 2005.

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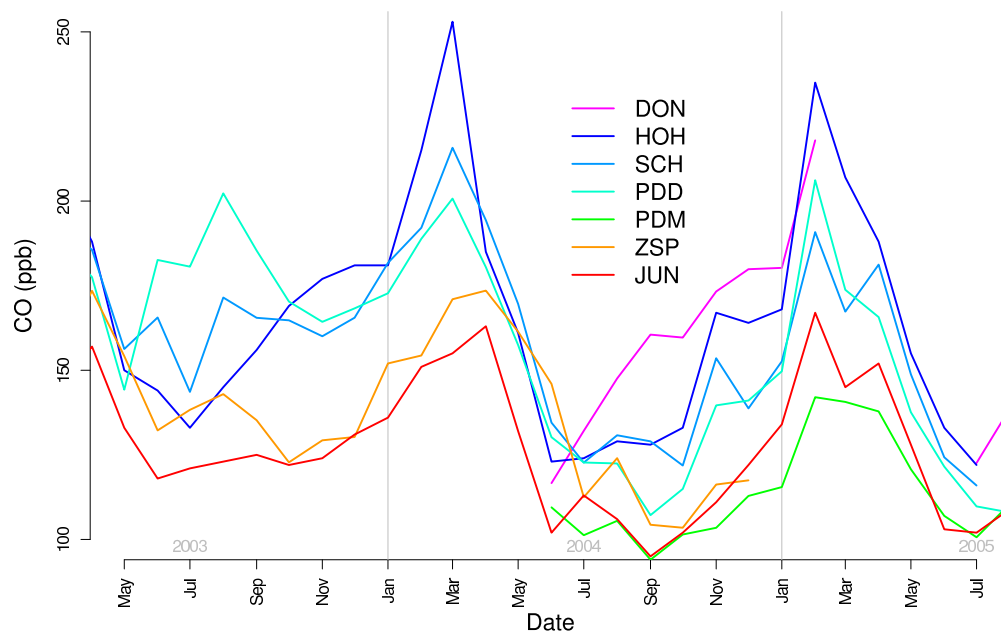


Fig. 4. CO monthly averaged mixing ratios at the seven stations between June 2003 and July 2005.

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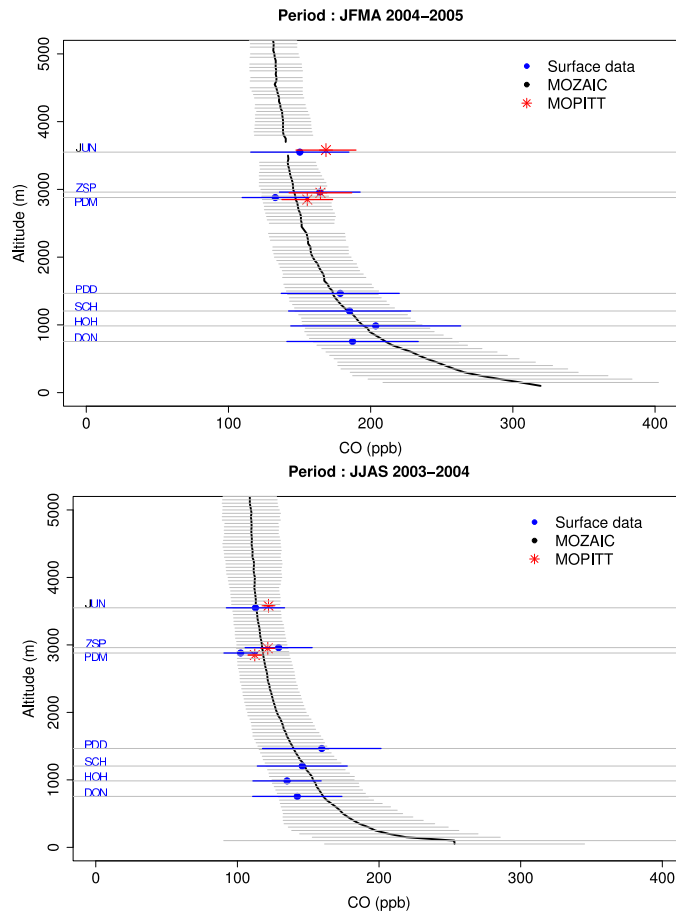


Fig. 5. As Fig. 3 but for seasons JFMA (2004+2005) and JJAS (2003+2004).

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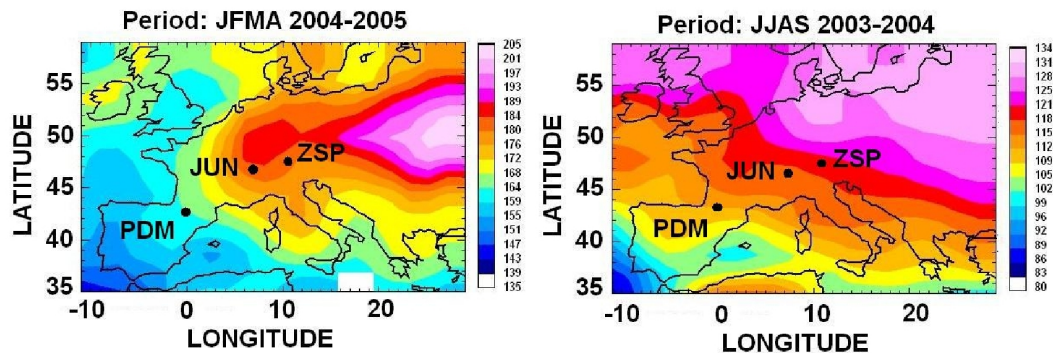


Fig. 6. CO concentrations (ppb) seen by MOPITT at 700 hPa over Europe averaged over the periods JFMA (2004 and 2005) and JJAS (2003 and 2004). For clarity, the colorscales are different in the two panels.

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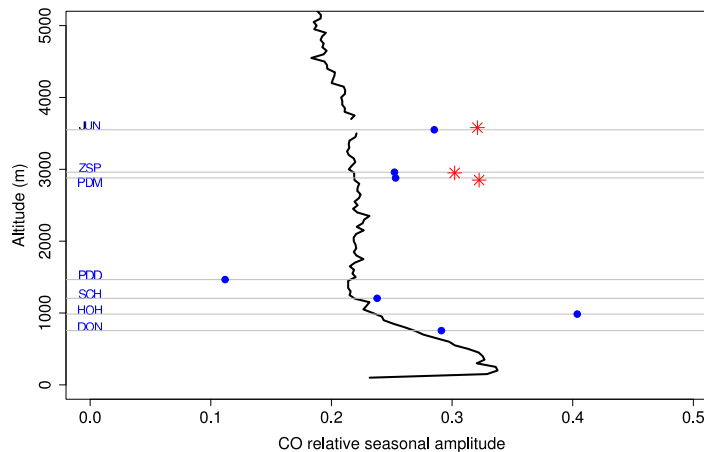
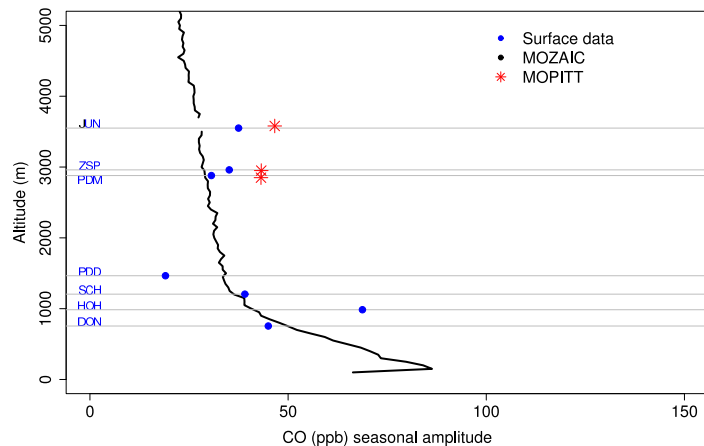


Fig. 7. (a) Seasonal amplitude and (b) relative seasonal amplitude as seen by MOZAIC, MOPIIT and surface data between JJAS 2003–2004 and JFMA 2004–2005 periods.

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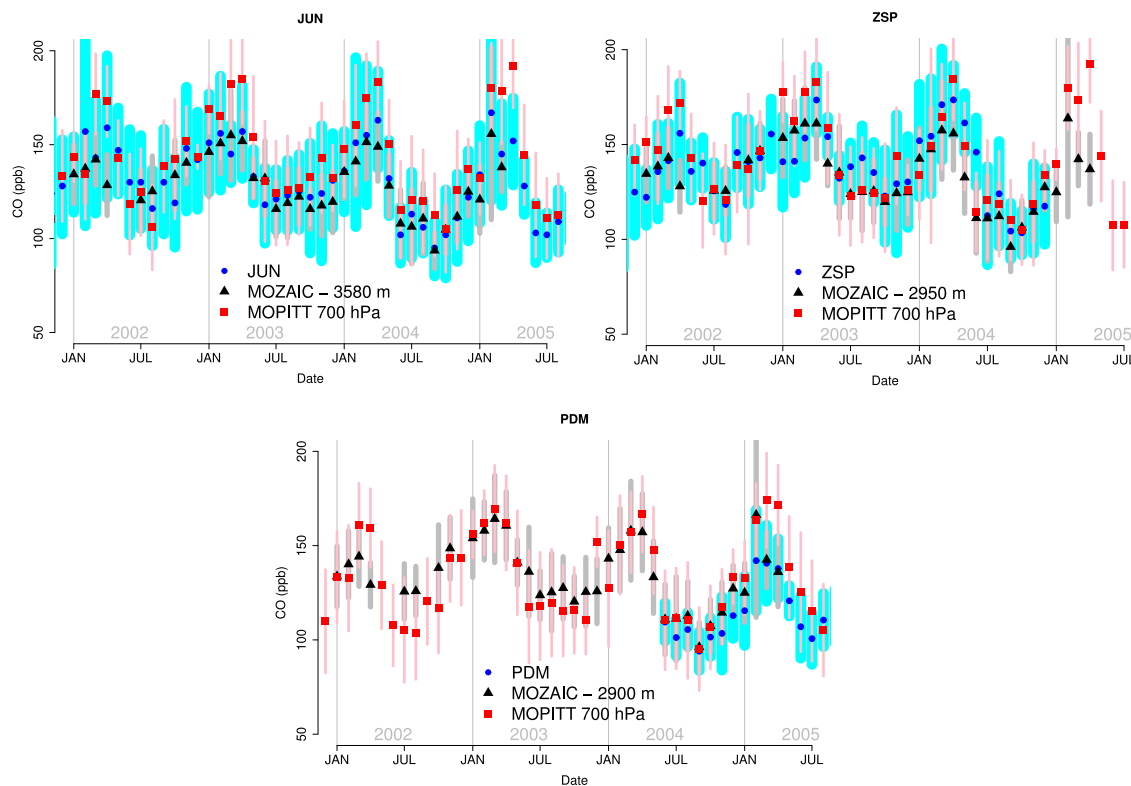


Fig. 8. Comparison of monthly mean CO (symbols) and corresponding standard deviation (bars) between surface data, MOZAIC and MOPITT data at 700 hPa for the highest stations (JUN, ZSP and PDM).

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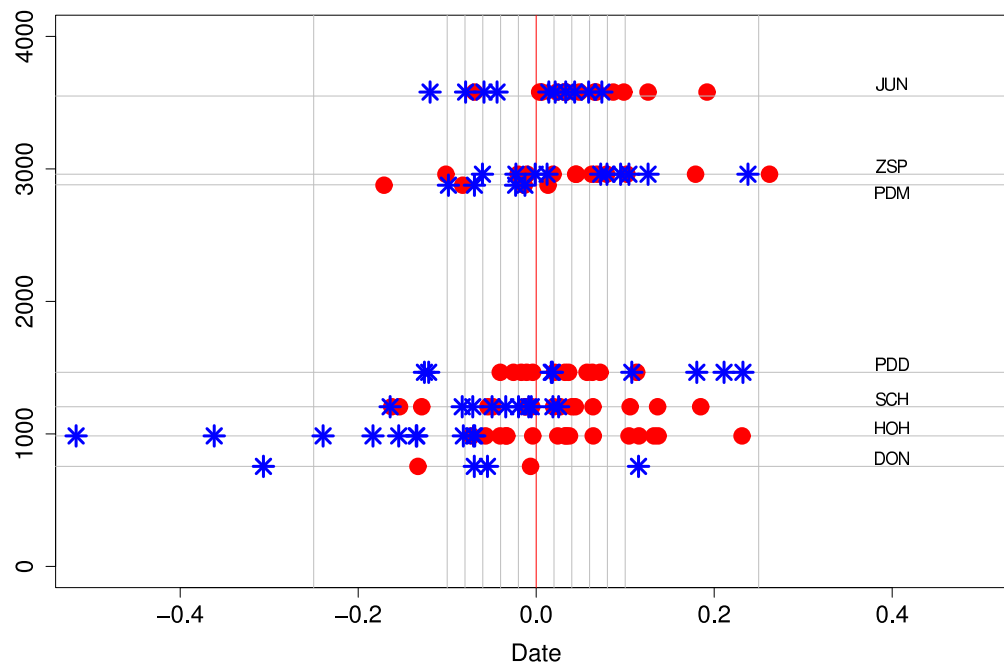


Fig. 9. Relative monthly deviation between MOZAIC and surface data (i.e. (surface-MOZAIC)/surface) for the JFMA (red) and JJAS (blue) periods between January 2002 and April 2005. (One point per month).

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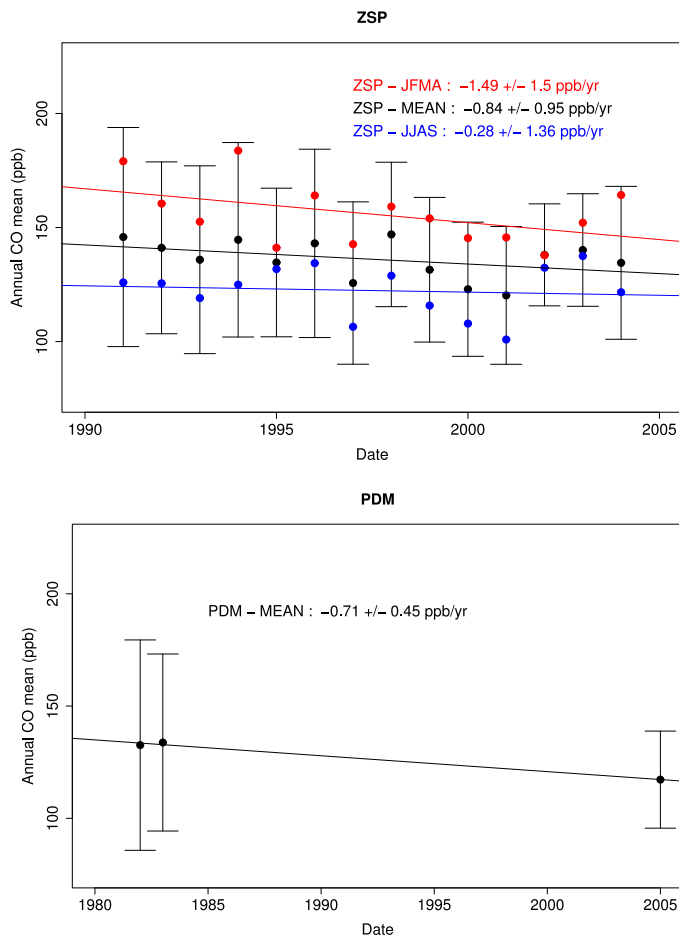


Fig. 10. Long-term trends in high-altitude stations at Zugspitze (ZSP, Germany) from the 1990s and Pic du Midi (PDM, France) from the early 1980s. Averages on annual, JJAS and JFMA periods are respectively presented in black, blue and red.

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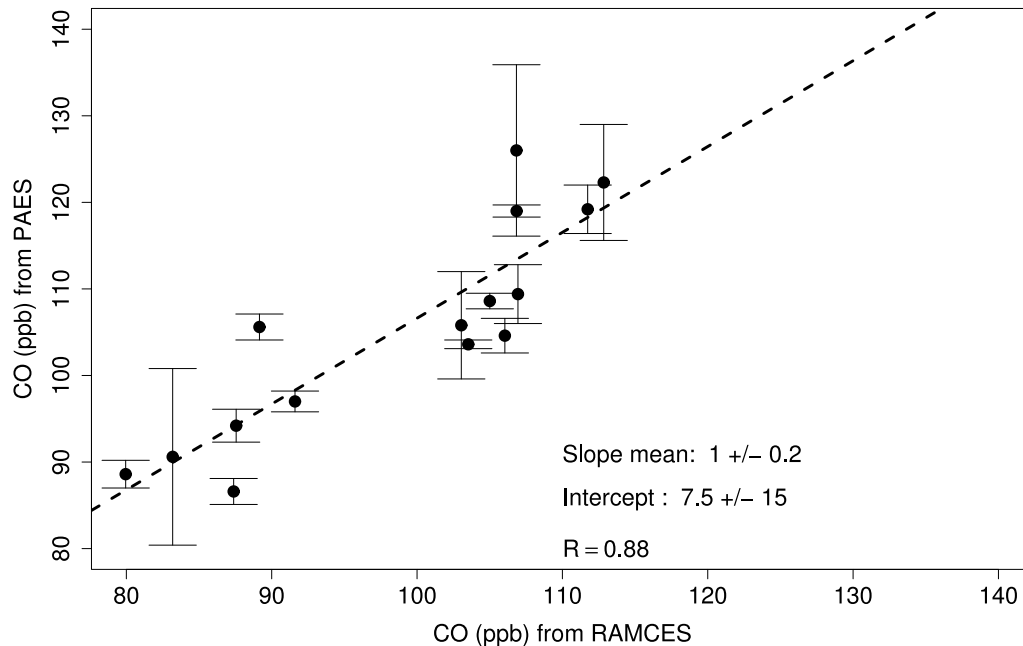


Fig. 11. Comparison between the two analytical technics used in 2005 at PDM: infrared CO analyzer used actually for PAES and chromatography used by RAMCES. PAES data are averaged on one hour around the RAMCES measurement times.

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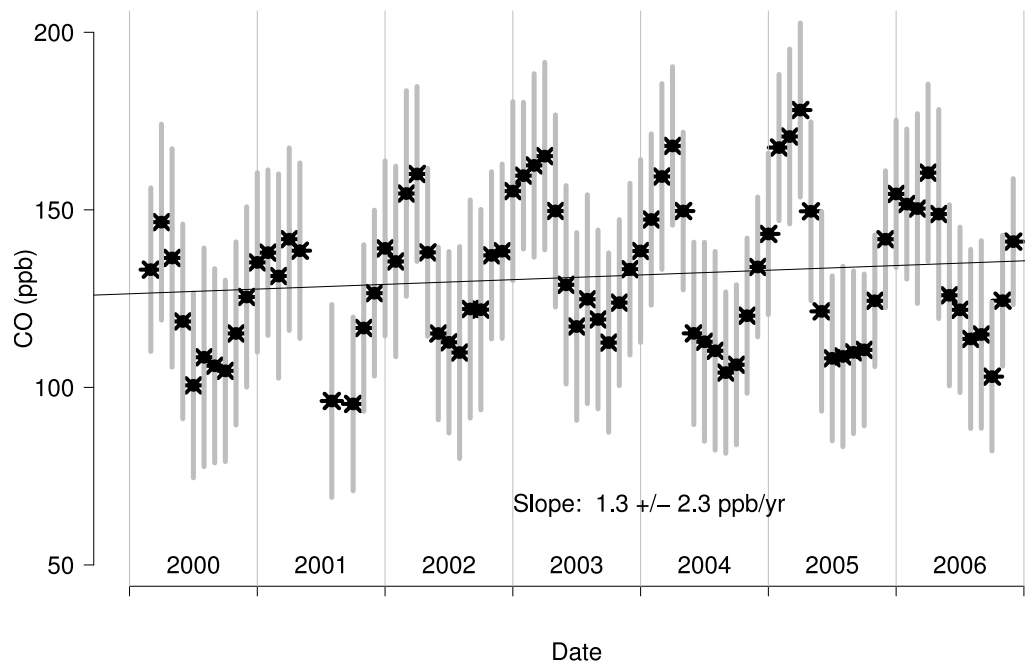


Fig. 12. Monthly mean CO concentration and estimated trend between 2000 and 2007 from MOPITT retrievals at 700 hPa on average over a 1500 km-radius area over Western Europe.

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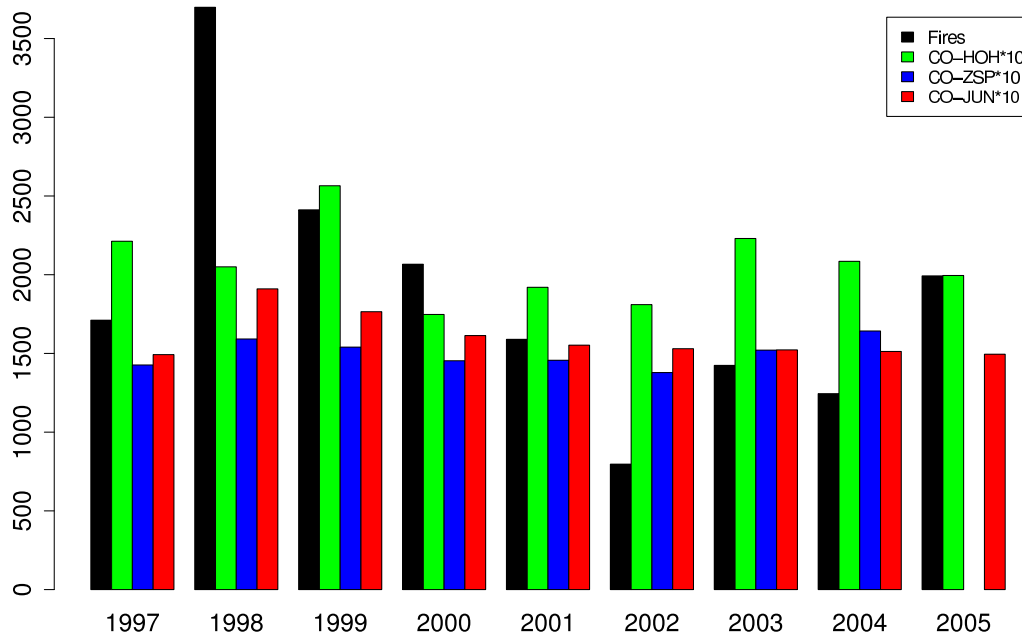


Fig. 13. Total number of fire pixels above Europe, Asia and North America during the JFMA period (black), compared to yearly mean CO concentrations (x 10 in ppb) at HOH, ZSP and JUN.

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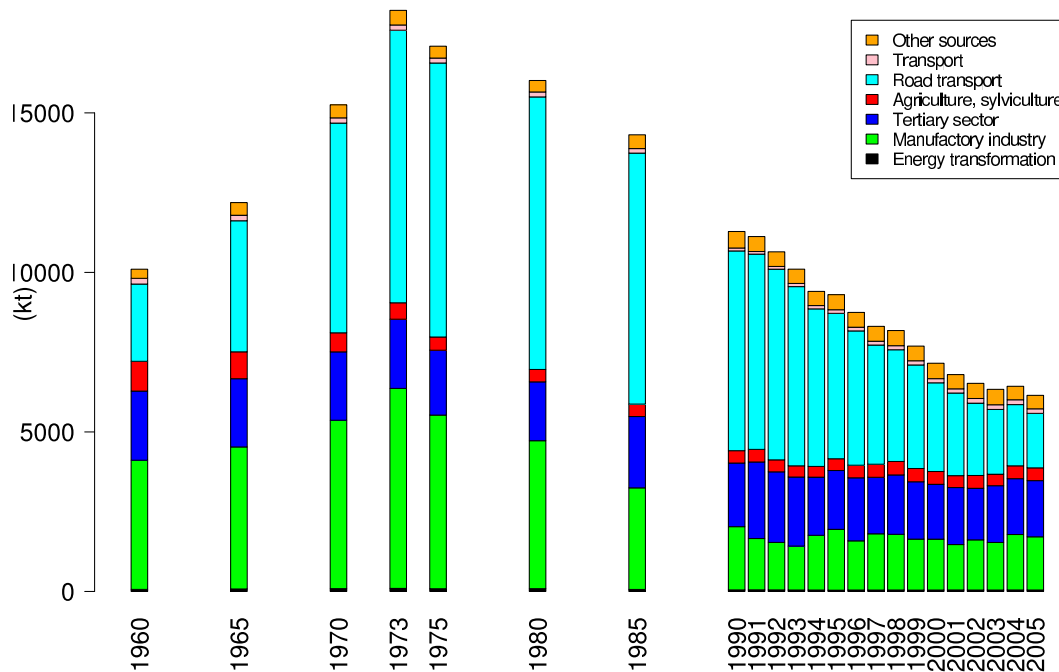


Fig. 14. Speciated CO emissions in France since the 1960s, and the 1990s. Source: CITEPA/CORALIE/format SECTEN (update from the 23 February 2006) available on <http://www.citepa.org>.

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