



Influence of atmospheric stability and transport on CH₄ concentrations in northern Spain



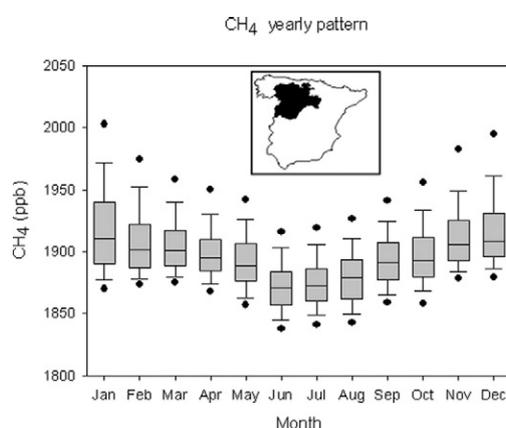
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HIGHLIGHTS

- Dry CH₄ concentrations obtained with a multi-point sampling system were analysed.
- Daily and yearly patterns were similar for the different heights.
- Air mass trajectories, mainly S-SE sectors, influencing CH₄ concentrations
- Conditions for background levels were established.

GRAPHICAL ABSTRACT



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ABSTRACT

Continuous methane (CH₄) concentrations were measured in Northern Spain over two years (2011–2012) by multi-point sampling at 1.8, 3.7 and 8.3 m using a Picarro analyser. The technique is based on cavity ring-down spectroscopy. The contrast in mean concentrations was about 1.2 ppb, with 95th percentiles differing by 2.2 ppb and mean minimum concentrations proving similar. Temporal variations of CH₄ were also analysed, with a similar seasonal variability being found for the three heights. The highest CH₄ concentrations were obtained in late autumn and winter and the lowest in summer, yielding a range of 52 ppb. This variation may depend on the active photochemical reaction with OH radical during a period of intense solar radiation and changes in soil conditions together with variations in emissions. Peak concentration levels were recorded at night-time, between 5:00–7:00 GMT, with mean values ranging between 1920 and 1923 ppb. The lowest value, around 1884 ppb, was obtained at 16:00 GMT. This diurnal variation was mainly related to vertical mixing and photochemistry. Therefore, CH₄ concentrations were also examined using the bulk Richardson number (R_B) as a stability indicator. Four groups were distinguished: unstable cases, situations with pure shear flow, transitional stages and drainage flows. The highest contrast in mean CH₄ concentrations between lower and upper heights was obtained for the transition and drainage cases, mainly associated to high concentrations from nearby sources. The impact of long range transport was analysed by means of 3-day isobaric backward air mass trajectories, which were calculated taking into account origins from Europe, Africa, the Atlantic Ocean and Local conditions. Assessment of the results showed the influence of S and SE wind sectors, especially with Local conditions associated

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with low winds. Finally, an estimation of the background CH₄ concentration in the study period provided an average value of about 1892 ppb.

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1. Introduction

Together with water vapour and carbon dioxide, atmospheric CH₄ is an important greenhouse gas. All of these impacts on the Earth's energy balance through infrared radiation absorption, have the ability to scatter energy, and are involved in photochemical reactions (Sasakawa et al., 2010). CH₄ is less abundant but is over 20 times more powerful than carbon dioxide (Baldocchi et al., 2012; Lelieveld, 2006). The mean tropospheric lifetime of CH₄ ranges between approximately 8 and 12 years, whereas for carbon dioxide it varies, averaging over 30 years (Dlugokencky et al., 2012; IPCC, 2007; Sonnemann and Grygalashvyly, 2014). Moreover, CH₄ is involved in atmospheric chemistry (Bergamaschi and Bousquet, 2008). The current CH₄ concentration level in the atmosphere ranges between 1.7 and 1.8 ppm, which is more than twice the level of the pre-industrial period (Baldocchi et al., 2012; Padhy and Varshney, 2000; Wuebbles and Hayhoe, 2002). This increase is caused by the imbalance between CH₄ sources and sinks and has been widely studied (Dlugokencky et al., 2003; 2009; Zhou et al., 2004), although it is not yet fully understood (Dlugokencky et al., 2012; IPCC, 2013; Kirschke et al., 2013). For about a decade, the increase in global CH₄ levels remained unnoticed. However, from 2007 to 2009 a further rise was observed (Kirschke et al., 2013; WMO, 2011). There are several major sources of atmospheric CH₄ of both anthropogenic and natural origin. Anthropogenic sources comprise biogenic sources like agriculture, landfills and waste processes which produced CH₄ because of the anaerobic decomposition of organic matter; enteric fermentation in livestock farming; biomass burning when incomplete combustion occurs; methane leaks occurring in the production, distribution and combustion of fossil fuels and during industrial activities. CH₄ is also released by natural processes including wetlands resulting from microorganism activity in anaerobic conditions and abundant organic matter; digestion processes in termites, and microorganisms living in the oceans (IPCC, 2007; Kong et al., 2010; Sasakawa et al., 2010; Tsutsumi et al., 2006; Wuebbles and Hayhoe, 2002). Approximately two thirds of all CH₄ is anthropogenic in origin and emissions are mainly from the Northern Hemisphere (Lelieveld, 2006). However, there are certain processes through which CH₄ is removed from the atmosphere, 90% of these occurring in the troposphere. Active oxidation reaction with the hydroxyl radical (OH) produces other species such as formaldehyde, carbon monoxide and ozone under certain levels of nitrogen oxide (Wuebbles and Hayhoe, 2002). The process is particularly rapid in summer due to the photochemical nature of the OH radical. To a lesser extent, other sinks are microbial uptake by soils and reactions with Cl and O in the stratosphere (Alvalá et al., 2004; IPCC, 2007; Zhang et al., 2014).

Systematic CH₄ concentrations have been measured since the 1970s (Khalil and Rasmussen, 1994; Zhou et al., 2004). There are numerous greenhouse gas measurement programmes all over the world reflecting a major effort to make high-quality data available and to provide better insights into the processes that control gas abundance in the atmosphere, pinpoint trends and understand spatial distribution as well as the link to climate change. Several measurement techniques have become available allowing continuous and discrete samples in different scenarios (Crosson, 2008; GLOBALVIEW-CH₄, 2009; Padhy and Varshney, 2000; Veenhuysen et al., 1998; Zhou et al., 2004). CH₄ concentrations are also influenced by atmospheric processes in the boundary layer which affect their transport and dispersion. Together with dispersion and atmospheric transport models, satellite observations improve our knowledge of CH₄ behaviour in the atmosphere as well as potential sources and sinks (Buchwitz et al., 2005; Worden et al., 2012;

Zhou et al., 2003), thus allowing background CH₄ levels to be established.

In 2010, continuous measurements of CH₄ began at the Low Atmospheric Research Centre, CIBA, in the upper Spanish plateau at three different heights. The measuring site is a crop land use area which also has short grass. The nearest main populated cities are some distance from the sampling site, approximately 24 and 40 km away. Coupled with the meteorological features, this makes it possible to assess the usefulness of the site for atmospheric research. Studies of other gases, particularly CO₂, have provided valuable information about their levels in Spain, extending coverage of Southern Europe (García et al., 2008; Pérez et al., 2009a, 2009b; Sánchez et al., 2010). Our Laboratory is also involved in the NOAA ESRL Carbon Cycle Greenhouse Gas (CCGG) cooperative air sampling network (www.esrl.noaa.gov).

The current paper seeks to present and analyse continuous measurements of atmospheric CH₄ in the upper Spanish plateau with a multi-point sampling system. The influence of atmospheric stability and air mass movements in CH₄ concentrations is also presented. The background CH₄ concentration at the measuring site is quantified by means of a data set selection in order to minimize the effect of different controlling factors.

2. Experimental method

CH₄ was continuously measured at a ground surface station, CIBA (latitude: 41°49'N; longitude 4°56'W; altitude: 845 m a.s.l.) from January 2011 to December 2012 (Fig. 1). The location is a semiarid rural area characterized by non-irrigated crops as a major land use. The main nearby anthropogenic sources are the cities of Valladolid (300,000 inhabitants), located 24 km away and Palencia (80,000 inhabitants), which is further away, 40 km. Another possible contribution impacting on CH₄ concentrations to be taken into account is an urban landfill situated in the southeast sector, some 20 km from Valladolid. The landfill's estimated annual CH₄ emissions were around 7 kt year⁻¹ in the study period (PRTR, 2012).

The analyser is based on cavity ring-down spectroscopy (CRDS), G1301, and was developed by Picarro Inc. The device evidences low drift (averaging 0.2 ppb per month) and high precision (inferior to 1 ppb) and requires little maintenance, being able to simultaneously measure methane, carbon dioxide and water. The technique is based on the principle of measuring the rate of exponential decay of light intensity inside the cavity. The concentration of each gas species is proportional to the area of the spectral features. Details of the operating principle may be found in Crosson (2008); Crosson, 2007). As regards CH₄, the greenhouse gas studied in this paper, equipment accuracy is 0.5 ppb at ambient concentration levels with a response time of five seconds. Data were then processed as semi-hourly mean values. The analyser software includes a valve sequencer to automatically control external solenoid valves to measure at 1.8, 3.7 and 8.3 m. The response presents high linearity with concentrations. However, the equipment was usually calibrated twice per month applying NOAA standards, which is considered an adequate period for verification purposes of quality in atmospheric measurements (Wastine et al., 2009). The concentration read by the analyser for each standard and the actual concentration were fitted to a straight line by means of linear regression analysis for each calibration. Concentrations from the analyser were converted to the final data using the equation of the previous calibration with the three standards. Slopes of linear fits were always to be around 1, with correlation coefficients close to 1. The total number of valid data was around 98% (34,359, 34,227, 34,220 data for the 1.8, 3.7 and 8.3 m

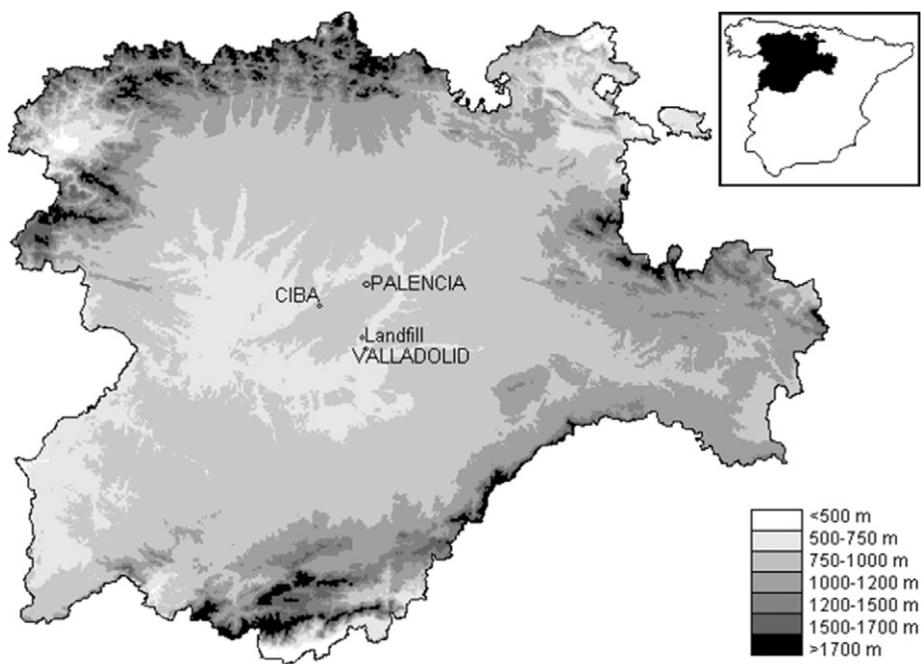


Fig. 1. Location of the sampling site, CIBA, on the upper Spanish plateau and the main CH₄ sources influencing the area.

levels, respectively), with missing data being mainly due to calibration procedures and power cuts.

A 10 m mast equipped with sensors to measure air temperature, wind speed and direction, and relative humidity was also installed at the site and data were recorded each 30 min. The climate at the measuring site is classified as continental Mediterranean. During the study period, it was featured by a mean wind speed of 3.5 m s⁻¹, ranging from 0.0 to 13.1 m s⁻¹. The prevailing wind directions using a 16-sector wind rose were NE, ENE, and WSW accounting for a frequency of 13.0, 11.7, and 10.8%, respectively (Fig. 2).

Temperature values ranged between -8.7 °C, recorded in December 2012, and 37.1 °C in August 2012, the average value being 11.5 °C.

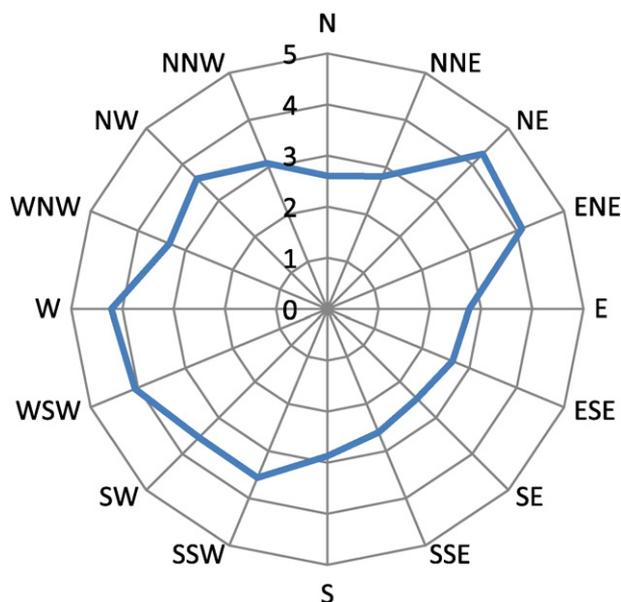


Fig. 2. 16-sector wind rose and the corresponding mean wind speed (m s⁻¹) during the measuring period.

Precipitation data were obtained from the Governmental Meteorology Agency (www.aemet.es). Maximum cumulative monthly precipitations were 65.5 and 99.6 mm in November 2011 and October 2012 (Fig. 3). Total recorded precipitation was 346.8 in 2011 and 387.5 mm in 2012. This study period corresponded to a drier period (mainly during the first year of study) compared to historical data, which showed mean yearly values (30 years) of around 450 mm.

3. Results

3.1. Water vapour correction

Water vapour content in the sampling air can underestimate CH₄ concentrations due to dilution, spectral line broadening variations, and nonlinearity of water vapour concentration (Wastine et al., 2009). This is discussed in Rella (2010) and the comparison of water correction factors from three research studies is also presented, although minor

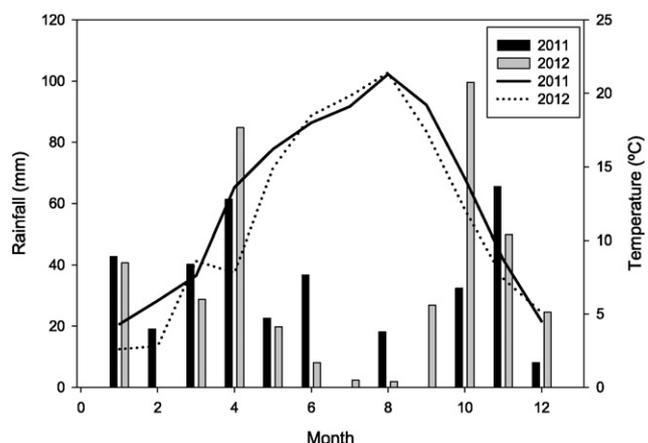


Fig. 3. Average monthly air temperature (line and scatter plot) and cumulative monthly precipitation (vertical bars) measured at CIBA in the study period.

differences emerge between them. The manufacturer has developed a correction equation for CH₄ measurements which takes into account water influence. The range of water vapour for our data set was 0.22–2.82%. Correction was quantified by comparing dry and wet CH₄ measurements. The second order polynomial regression model fits the data well.

$$\frac{\text{CH}_4_{\text{wet}}}{\text{CH}_4_{\text{dry}}} = 1 - 0.00982\text{H}_2\text{O} - 0.000239\text{H}_2\text{O}^2 \quad (1)$$

with a coefficient, $R^2 = 1$ and a residual mean square, $\text{MS}_{\text{Res}} = 4.7 \times 10^{-10} \text{ ppb}^2$. This paper deals with dry CH₄ concentrations, which presented small errors due to water vapour correction.

3.2. Temporal variations of CH₄

An overall view of CH₄ concentrations for the three heights considered in the study period was performed. Methane concentrations showed small differences in air during the measuring period (Table 1). That is, mean concentrations increased only slightly with height and standard deviations were similar for the three levels, indicating stability. The difference between the 1.8 and 8.3 m levels was 1.3 ppb for mean concentrations. The two upper level medians differed by around 1 ppb from that of the lower one. The highest methane concentrations were found at a height of 1.8 m, mainly corresponding to outliers since the values were three times higher than the interquartile range from the upper quartile. Minimum concentrations were around 1813 ppb for the three heights. Differences with values at 3.7 m height were not significant, 0.5 ppb, the maximum differences being 0.9 ppb for the 90th and 95th percentiles. A greater contrast was in evidence with the 1.8 m height. The 95th percentile differed by 2.2 ppb and the 98th percentile by 4.5 ppb. The other percentiles were around 1.2 ppb less (Fig. 4).

Seasonal evolution showed temporally defined patterns. The monthly mean evolution of CH₄ concentrations for the greatest height (8.3 m) is depicted in Fig. 5. Maximum mean concentrations were seen in late autumn, December and January, and averaged around 1924 ppb. Concentrations then decreased in spring and summer.

Changes in CH₄ sources and sinks, temperature and soil moisture conditioned absorption at this time of the year, contributing to the cycle and therefore to seasonal amplitude (Mu et al., 2006; Zhou et al., 2004). The lowest mean values were obtained in June and July, and averaged around 1875 ppb. This might be attributed to higher temperatures, which dry the croplands and the later harvest, and consequently weak plant activity. This temperature and moisture dependency might lead to an increase in CH₄ uptake (Mu et al., 2006). The oxidation process of CH₄ with the OH radical was also more intense in spring and summer since OH is a photochemical species reaching its maximum concentrations (Dlugokencky et al., 2009). The height of the mixing layer, which is high in summertime, contributes to the dilution of components in the atmosphere and gives rise to lower CH₄ concentrations. The monthly evolution described for the upper height was similar to that described for the other heights. Monthly cycle amplitudes, as the difference between the maximum and minimum mean values, were 52.1, 52.3 and 51.7 ppb for the 1.8, 3.7 and 8.3 m heights, respectively,

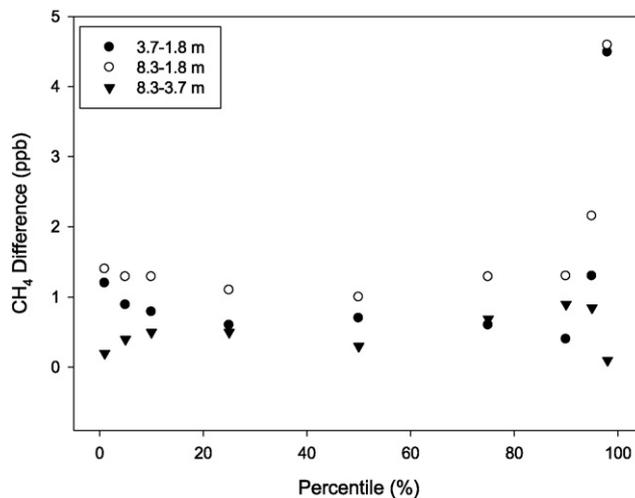


Fig. 4. Differences between the CH₄ percentiles of the various measurement heights.

which are in the range of those provided for locations in the Northern Hemisphere (Crevoisier et al., 2013). Consequently, CH₄ concentrations by season at the various sampling points correlated significantly with each other ($R^2 > 0.8$). This 8.3 m height was taken as a reference and differences with the other heights were calculated. As a result, the greatest differences might occur mainly in periods with lower precipitations or with higher temperatures linked to low soil activity, although these did not exceed 2.4 ppb (Whalen, 1993). In addition, when the medians of the monthly concentrations were considered, ranges of the yearly cycle were around 39 ppb for the three heights. The two upper heights showed practically no differences. The daily average median values for each season of the year showed more accentuated amplitudes in spring and summer, 28.9 and 32.5 ppb, respectively. However, in winter and autumn they were much lower 23.3 and 21.1 ppb, respectively. This could be attributed to the higher/lower range of CH₄ concentrations during the day, respectively, which might be associated to photochemical reactions, other environmental factors or even the variable intensity of CH₄ emissions.

Further analysis of atmospheric CH₄ concentrations has evidenced the enormous variability of its diurnal pattern; concentrations generally tending to increase at night-time and decrease in daytime. Fig. 6 shows hourly mean CH₄ concentrations. During the day, from 8:00 to 18:00 GMT, concentrations were nearly the same for the three levels considered. Minimum mean values were recorded at 16:00 GMT, 1883.9, 1884.1 and 1884.1 ppb at 1.8, 3.7 and 8.3 m, respectively. These results

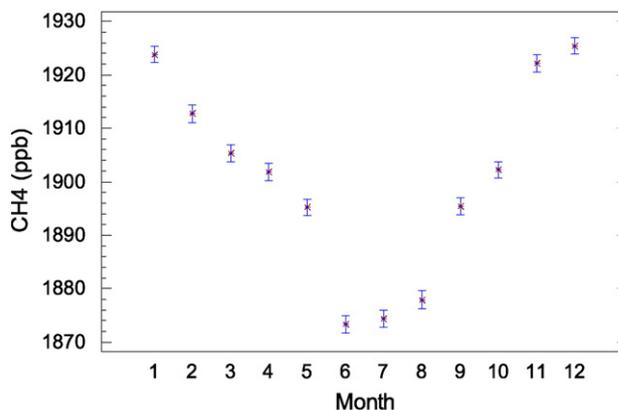


Fig. 5. Monthly evolution of dry mean CH₄ concentrations at 8.3 m. The least significant difference intervals (95% confidence level) are also depicted.

Table 1
Main statistics of CH₄ concentrations at the three different heights.

Height (m)	Mean (ppb)	Median (ppb)	Standard deviation (ppb)	Maximum (ppb)	Minimum (ppb)
1.8	1900.9	1892.6	64.5	4777.6	1812.6
3.7	1901.8	1893.3	65.8	4452.6	1812.6
8.3	1902.2	1893.6	63.9	4661.6	1813.2

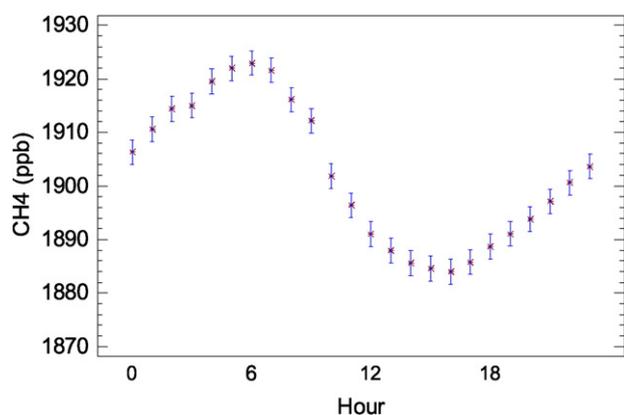


Fig. 6. Daily evolution of dry mean CH₄ concentrations at 8.3 m height. The least significant difference intervals (95% confidence level) are included.

were mainly associated with the reactions involving OH radicals depending on temperature and solar radiation (Vaghjiani and Ravishankara, 1991). Moreover, CH₄ concentrations are regulated by thermal turbulence, which causes intensive vertical mixture. The height of the mixing layer varied with a maximum during the day causing lower concentrations since there was more dilution in the air (Sasakawa et al., 2010; Pérez et al., 2012). As regards mean median values at this time, there were no differences between the two upper levels and the lowest level, 0.3 ppb. The higher concentration at night-time can be explained by the collapse of the boundary layer, an increase in atmospheric stability and elevated methane emissions related to fugitive emissions from landfill activity. Strong temperature inversions at the site also contributed to trapping gases at night-time (Baldocchi et al., 2012; Sánchez et al., 2010).

Slightly higher differences between the concentration measured at 8.3 m and at the low height, 1.8 m, were found overnight when

concentrations are greater, and averaged around 2.3 ppb. This behaviour can also be seen in the medians, 1.9 ppb. The daily range was around 38.6 ppb for 1.8 m, and 39.1 ppb for the 3.7 and 8.3 m heights. Maximum concentrations were obtained at 5:00–7:00 GMT for the three levels showing a difference of 2 ppb between the two upper levels, with an average close to 1923 ppb, and the lowest. This daily cycle was similar to that obtained in other environments (Baldocchi et al., 2012; Gao et al., 2011).

When the CH₄ diurnal pattern for each season in the study period was considered, a similar behaviour of mean CH₄ concentrations was obtained for all the heights in winter, spring, summer and autumn. The evolution pattern for the 8.3 m height can be seen in Fig. 7(a–d). In winter, an amplitude of 31.8 ppb in the mean values was observed whereas in spring, the diurnal range was higher, 49.5 ppb, with values gradually increasing from 16:00 to 5:00 GMT when a peak was reached. A similar diurnal pattern was obtained in summer although with a lower amplitude, 44.2 ppb. In autumn, the range is 51.1 ppb and higher values were recorded during the early morning, showing a greater contrast than the increasing evolution in the other seasons. Seasonal and diurnal changes in the boundary layer and nocturnal inversions, atmospheric transport, photochemical reactions in warm seasons and soil features conditioned the CH₄ evolution found during the measurement period. Results were in agreement with those observed at other continental sites in the Northern Hemisphere (Dlugokencky et al., 1993) and differed from other unusual patterns (Zhou et al., 2004).

3.3. Atmospheric stability

The evolution of the boundary layer is strongly related with variations of components in the atmosphere. In this section, the effect of atmospheric stability on CH₄ concentrations at the sampling location is examined. The bulk Richardson number (R_B) has been widely used to specify dynamic stability and turbulence and has been successfully applied to classify wind speed profiles (Komatsu et al., 2005; Pérez et al., 2009a). The bulk Richardson number is defined following the same

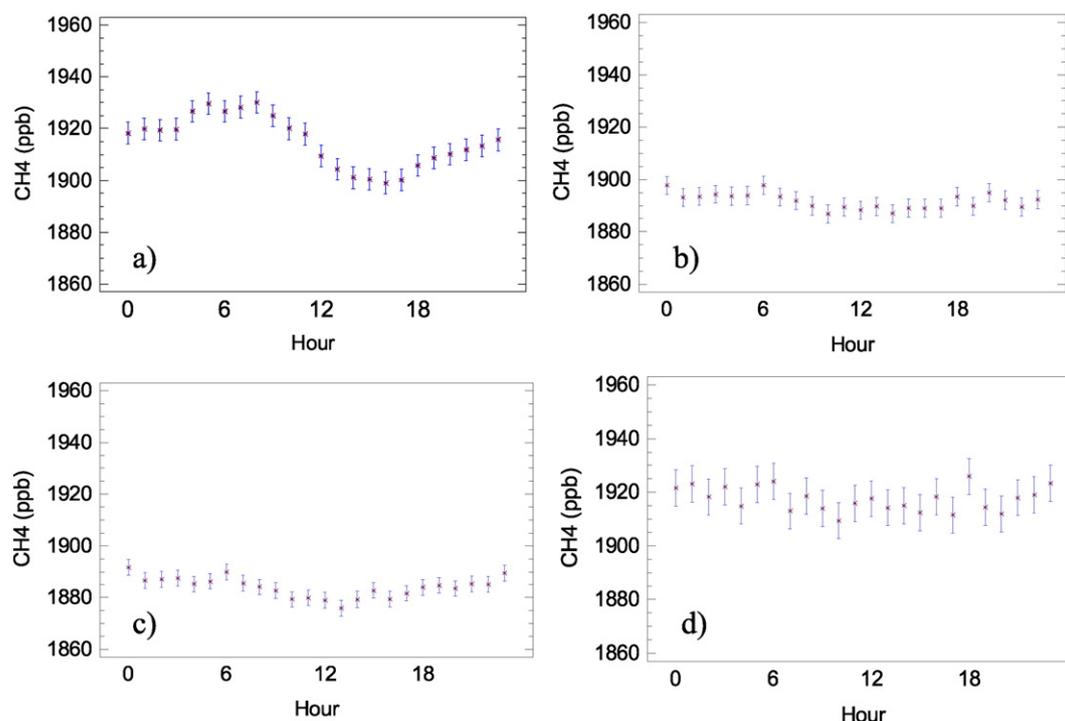


Fig. 7. Daily pattern of dry mean CH₄ concentrations by season for the 8.3 m height in the study period: a) winter; b) spring; c) summer; and d) autumn. Intervals with the least significant differences (95% confidence level) are drawn.

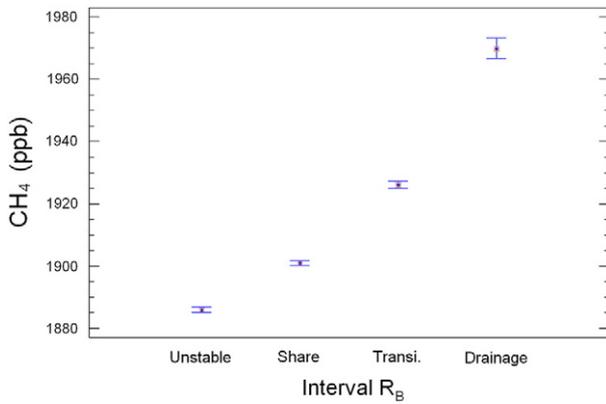


Fig. 8. CH₄ means at 8.3 m height for the stability groups: Unstable, Pure shear, Transi. (Transition) and Drainage. Intervals with the least significant difference are also depicted (95% confidence level).

procedure as Pérez et al. (2009b) taken from Arya (2001),

$$R_B = \frac{g z}{T} \frac{(\theta - \theta_s)}{u^2} \quad (2)$$

where g is acceleration by gravity, T is air temperature at 34.6 m, u is wind speed at 34.6 m, z is the reference height, and $\theta - \theta_s$ is the difference between the potential temperature at 34.6 and 10 m. We were seeking an empirical relationship between wind profiles represented by relative wind speed and atmospheric stability linked to R_B . Relative wind speed was analysed as a function of the R_B and different intervals could be established. In this study, it was set at $R_B < 0$ for neutral or unstable cases, mainly from daytime data; $0 < R_B \leq 0.05$ for pure shear flows; $0.05 < R_B \leq 0.5$ includes transition stages; and $0.5 < R_B$ for drainage flows associated to stables cases, most of them from night-time values.

Mean CH₄ concentrations at 8.3 m, as the reference height, were calculated for each interval. An analysis of the variance between CH₄ concentrations and the intervals of R_B values distinguished four groups with means whose differences are statistically significant at 95% confidence level. Fig. 8 depicts CH₄ means at 8.3 m for the different stability groups. In addition, Table 2 shows CH₄ means and medians together with the meteorological variables characterizing the groups. Fig. 8 shows how unstable situations corresponded to lower concentrations, on average 1885.8 ppb, since these observations were recorded during the day, and accounted for 99.2% of the data in this group. They were linked to days with high relative wind speed, a mean value of 4.3 m s⁻¹ and an average temperature of around 18 °C. In addition, diurnal convection causes the air to rise to high altitudes, such that this result should be considered as background concentration considering only daytime, yielding a mean value of about 1885 ppb. The second group, including pure shear flows, with a mean wind speed of 3.9 m s⁻¹, showed a higher CH₄ concentration, 1901 ppb. The next group corresponded to transition situations, mainly at night and with inhibited vertical movement, an average of 1926 ppb, with lower mean wind speed, 1.9 m s⁻¹. Drainage cases with high R_B values, low relative wind speed, 0.8 m s⁻¹ and temperature about 3 °C, yielded a mean CH₄ value of 1969.9 ppb,

although the frequency of these observations at this site with no complex terrain was the lowest, standing at 2%.

We now focus attention on the differences between CH₄ concentrations at the 1.8 and 8.3 m heights. The highest contrasts in their means were obtained for the transition and drainage cases during the night, 4 and 7 ppb, respectively, associated to low winds and temperatures as main features. However, in order to avoid the influence of outliers or extreme values influencing these two groups, medians of CH₄ concentration values were considered. The first two groups contained the greatest number of cases, approximately 76% of the whole, and showed a median value of 1883 and 1895 ppb, respectively, with CH₄ concentrations being almost homogeneous within these heights. In the third group, medians showed a slight difference between low and high heights, 1905 and 1908 ppb, respectively. The influence of extreme values was particularly important given the difference between the average values and the median data, around 17 ppb for all the heights and occurred in 21% of cases. For drainage flows, a greater difference was found in the medians, 6 ppb, 1922 and 1928 ppb for the 1.8 and 8.3 m height, respectively. Compared with the mean values shown in Table 2, outliers might contribute with around 42 ppb. These situations may be attributed to high emissions from nearby sources, mainly the cities of Valladolid and Palencia and the urban landfill. Consequently, atmospheric stability as a function of R_B proved useful to differentiate CH₄ concentrations at a specific location.

3.4. Trajectory analysis

The impact of anthropogenic emissions and natural processes on CH₄ concentrations at the sampling site was also investigated in response to atmospheric transport pathways which represent one of the main controlling factors of greenhouse gases (Artuso et al., 2007; Balzani et al., 2008). For this reason, this effect was analysed by means of the air-flow patterns of back-trajectories. The origins of the advected air masses reaching the sampling site for each of the measuring days were tracked. Trajectories were obtained using the HYSPLIT-4 Model (Hybrid Single-Particle Lagrangian Integrated Trajectory) (Draxler and Rolph, 2014; Rolph, 2013). This model has been successfully applied in many studies assessing the influence of long-range transport on high ambient pollutant concentrations (Cristofanelli et al., 2011; García et al., 2005; Van der Laan et al., 2009). A mixed layer where transport and dispersion take place is assumed by the model. The vertical extent of the mixed layer is calculated within the model from potential temperature data by finding the height of an elevated inversion at each grid point. Three day (72 h) backward trajectories originated at 06:00 GMT and, taking an arrival height of 500 m above ground level, were calculated by the model. This height was selected since it could be representative of the top of the transport layer and it is commonly taken as a boundary between surface and upper winds (Katsoulis, 1999). These trajectories were first used to analyse dry CH₄ concentrations in the study period at the upper height as the reference of the whole range.

Wind sectors were assigned to each of the back-trajectories taking into account the beginning of the trajectory. Trajectories were classified into four origins (Fig. 9): Atlantic (air masses originating in the sectors between the northwest and southwest of the Atlantic Ocean); European (air masses commencing at some location over Europe and

Table 2
Mean and median CH₄ concentrations and meteorological variables for the stability groups at 8.3 m height using the bulk Richardson number.

	Frequency (%)	Mean CH ₄ (ppb)	Median CH ₄ (ppb)	Wind speed (m s ⁻¹)	Temperature (°C)
Unstable cases	31.8	1885.8 ± 35.1	1883.0	4.3	17.6
Pure shear	45.4	1900.9 ± 43.7	1895.1	3.9	9.1
Transition stages	20.6	1926.0 ± 95.7	1908.2	1.9	7.4
Drainage flows	2.3	1969.9 ± 195.7	1927.6	0.8	3.1



Fig. 9. Map of the trajectory origins with the sampling point in the centre. Local trajectories are confined to the Iberian Peninsula.

reaching the sampling site from northeast to southeast); African (trajectories originating in the African continent and entering the Peninsula from the south, southwest, or southeast); Local (air masses are confined within the Iberian Peninsula or its vicinity and travel short distances).

The main results are presented in Table 3 for the study period. The dominant trajectories were Atlantic, accounting for 53.3% particularly in spring, summer and autumn. Conversely, an African origin was infrequent, presenting the smallest ratio, 5.4%. Daily maximum CH₄ concentrations showed the highest mean value compared to the other origins and were influenced by variations in emissions/uptake, environmental and meteorological factors. Atlantic and European trajectories provided the smallest average values, 1974 and 1990 ppb, respectively. However, Local conditions together with African trajectories presented the highest average maxima, 2058 and 2171 ppb, respectively. This result could be interpreted bearing in mind that the location of the main pollutant sources lies in the surroundings or inland (Europe) and stagnant conditions. Smaller discrepancies were found for the average minimum concentrations, with a range between 1863 and 1885 ppb. However, mean values were around 1910 ppb for all the trajectories except for those of Atlantic origin, which had 15 ppb less. The marine boundary layer might also act, albeit to a lesser extent, as a sink due to chlorine radical reactions (Kirschke et al., 2013). These results were in accordance with those reported in other studies such as Mauna Loa (Harris et al., 1992). However, contrasting results were obtained by Zhang et al. (2013) at locations in China.

Further analysis of CH₄ concentrations was performed by taking into account wind direction and speed during the whole day. Considering the 16 sectors of the wind rose, 22.5° each, the results showed the great importance of the S, SE and SSE in the CH₄ concentrations recorded at CIBA, together, although to a smaller degree, with ESE and SSW. The influence of these wind directions in CH₄ variations was also discussed in Sánchez et al. (2014). The overall mean value of CH₄ concentrations in the previously mentioned wind sectors was 1924.7 ppb, approximately 31 ppb higher than that of the remaining sectors. Specifically, the results obtained for the days associated with Local conditions provided a 95th percentile of 1979.4 ppb. The group including S, SE and SSE presented a frequency of 19.9%, with an average concentration of 1945.0 ppb, the lower quartile being 1891.1 ppb and the interquartile

range 57.7 ppb (Table 4). The mean wind speed associated for the Local conditions was 2.6 m s⁻¹, with 60% of the data being lower, which represented a light wind on the Beaufort scale. As a consequence, sources, mainly nearby cities, the landfill and livestock which lie in those directions, might make a greater contribution to CH₄ levels. Exceedances of the said CH₄ threshold (95th percentile) may be ascribed to singular fugitive emissions from the nearby sources, particularly from the landfill, on average 2140.8 ppb.

As regards days assigned to African trajectories, these provided a 95th percentile of 2015.5 ppb. The main wind directions of interest presented a lower interquartile range, around 12 ppb less than that of the Local conditions and with an average wind speed of above 3 m s⁻¹. The average of the greatest concentrations considered as exceedances was 2287.5 ppb, although these were infrequent. The difference between maximum and minimum values of African origin was higher than in the others and might be due to sporadic fugitive emissions in the main direction of the source influence, although there were few values such that no definite conclusion could be established.

When days with European trajectories were isolated, results showed that the 95th percentile was 1957.5 ppb and the average for exceedances is 2075.5 ppb. The higher values obtained for the Local conditions and African trajectories (less frequent) were influenced by the impact of nearby anthropogenic sources, sporadic emissions, a greater frequency of the southeast wind sector and the state of the lower atmosphere at the measuring site. The European origin comprised fewer cases involved within the S and SE sectors, 10%, which provided an

Table 3
Main CH₄ results corresponding to the 8.3 m height for each trajectory.

Trajectory	Frequency (%)	Maximum (ppb)	Minimum (ppb)	Mean (ppb)
Atlantic	53.3	1973.5	1871.9	1894.9 ± 35.4
European	19.1	1990.4	1885.3	1910.8 ± 25.2
Local conditions	22.2	2058.1	1876.9	1911.2 ± 46.4
African	5.4	2171.1	1862.7	1909.5 ± 48.5

Table 4
95th percentile for each trajectory. Influence of the main wind sectors, S, SE, SSE through different statistics: lower quartile, interquartile range and exceedances.

Origin/statistics	95th (ppb)	Lower quartile (ppb)	Interquartile range (ppb)	Exceedances (ppb)
Local conditions	1945.0	1891.1	57.7	2140.8
African	2015.5	1883.7	45.5	2287.5
European	1957.5	1892.2	49.5	2075.5
Atlantic	1945.4	1887.3	44.6	2073.0

average concentration of around 1937 ppb with some influence from continental sources. Wind directions, NNE, NE and ENE represented 55% of all cases within the days with European trajectory, with mean CH₄ concentrations being around 1908 ppb, a value similar to the mean found for this type of trajectory. The mean wind speed for all days was 3.7 m s⁻¹, higher than that for Local conditions and African trajectories. Regarding the Atlantic trajectories, the 95th percentile is 1945.4 ppb and the average for the exceedances is 2020.2 ppb. Cases with wind directions involved in the W, NW and N sectors were 46%, with a mean CH₄ value of 1889.5 ppb, around 2 ppb higher than the lower quartile. SE and S sectors with a lower frequency, 9%, were associated with a mean concentration of 1931 ppb, linked to a mean wind direction of 2.5 m s⁻¹. From the results, the important contribution of source emissions around the sampling site on CH₄ concentrations can be concluded, together with the dominant air flow, particularly S, SE, SSE wind directions, especially with Local conditions associated to low winds.

3.5. The CH₄ background concentration

The results obtained in the previous subsections regarding temporal variations, exceedances and transport were suitable for determining the representative conditions of the background CH₄ level at the site in a well-mixed air, in an effort to distinguish the contribution of potential sources of interference and to avoid concentration excess. To analyse the state of CH₄ in the atmosphere it was important to separate the data affected by local conditions or neighbouring sources from those in undisturbed conditions. There were different procedures for selecting data (Zhou et al., 2004). First, data from 8.3 m height were selected for this analysis due to the similar behaviour between the different levels and that height is comparable to the measurement height of the meteorological variables. In our case, data were representative of baseline conditions without considering the following values: all CH₄ values associated with winds from the SE and S sectors (ESE, SE, SSE, S and SSW) (22.6%), and values during calms which referred to stagnant local conditions (1.1%). Moreover, different restrictions were taken into account to exclude data: a) values outside the mean $\pm 3\sigma$ (σ is the standard deviation of all data, 64.1 ppb) so as to avoid peaks from high emissions, 0.29% of data; b) values outside the mean $\pm 1.5\sigma$, approximately 0.93%; c) values above the 90th and below the 1st percentiles (8.45% of all data); d) values above the 75th and below the 1st

percentiles (21.97%); and finally, e) values above and below the interquartile range (IR) from the upper and lower quartile, 1955.5 and 1849.3 ppb, respectively (3.84%). The remaining data in each case provided mean CH₄ values which are presented in Table 5. The range of mean concentrations obtained was 10.2 ppb. The lowest mean value corresponded to the restriction using the 1st and 75th, 1884.1 \pm 17.0 ppb, and the highest value was obtained with the mean $\pm 3\sigma$, 1894.3 \pm 29.2 ppb. Consequently, in order to establish a background level for CH₄, the three remaining mean values were considered, although restrictions b) and d) yielded similar values, with a difference of 0.2 ppb. Mean concentrations ranged from 1889.9 to 1893.2 ppb, and averaged around 1892.2 ppb, which is higher than others found for non-polluted areas (Sánchez et al., 2014). This value was closer to the concentration obtained after applying the restriction of mean ± 1.5 times the interquartile range or mean ± 1.5 times the standard deviation. The difference between the CH₄ baseline and the overall mean value from the whole data set was 10 ppb, and was therefore attributed to mainly anthropogenic sources such as cities, livestock and the landfill in the area together with the features of the lower atmosphere at the measuring site.

4. Conclusions

Dry continuous measurements of CH₄ concentrations over two years were carried out at three different heights, 1.8, 3.7 and 8.3 m, in a rural site at CIBA, on the upper Spanish plateau. An analysis of the variability of CH₄ concentrations was performed. In general, small differences in CH₄ concentrations were found for all heights, 2.3 ppb in the 95th percentile, presenting similar patterns. Monthly means increased from autumn to winter. Minimum concentrations occurred in June–July, with temperature being a significant controlling factor since it diminishes plant activity in the area, and methane oxidation with OH radicals intensifies, which is considered the principal removal process. The cycle peak-to-peak amplitude was about 52 ppb for the mean values, although the value is lower when medians are considered, 39 ppb. The daily pattern showed the lowest levels in the afternoon at 16:00 GMT, with a value of 1884 ppb, whereas the highest ones occurred over a wide range, from 5:00 to 7:00 GMT, with an average value of around 1923 ppb. This variation was related to changes in the mixing layer and in atmospheric turbulence and photochemical activity during the day and strong nocturnal inversions at night. R_B was used to analyse the influence of atmospheric stability on CH₄ concentrations. Four intervals were considered: unstable cases, pure shear flows, transition cases and drainage flows. When analysing them, we found the highest mean concentration for drainage flows, around 1970 ppb, with relatively high concentrations corresponding to transitional cases yielding 50 ppb less. Pure shear and unstable situations were linked to the lowest concentrations, 1900 and 1885 ppb, and the higher wind speed.

Although the computation methods provided a certain qualitative approach, analysis of the 3-day backward trajectories allowed us to distinguish the impact of air masses on CH₄ features, providing meaningful information of its variability in the atmosphere. Air masses over the sampling site from the Atlantic did not contribute to increasing CH₄

Table 5
Mean CH₄ concentrations once different selection criteria were applied.

Data excluded		Mean CH ₄ value (ppb) (1.8 m height)	Mean CH ₄ value (ppb) (3.7 m height)	Mean CH ₄ value (ppb) (8.3 m height)
• Calm conditions	a) Mean $\pm 3\sigma$	1893.1 \pm 29.1	1893.7 \pm 29.1	1894.3 \pm 29.1
• Wind sector influence (ESE, SE, SSE and S SSW directions)	b) Mean $\pm 1.5\sigma$	1892.3 \pm 27.3	1892.9 \pm 27.3	1893.4 \pm 27.2
	c) 1% < data < 90%	1888.7 \pm 21.2	1889.3 \pm 21.1	1889.9 \pm 21.1
	d) 1% < data < 75%	1882.9 \pm 17.1	1883.6 \pm 17.0	1884.1 \pm 17.0
	e) Mean ± 1.5 times the interquartile range	1892.2 \pm 22.2	1892.7 \pm 22.1	1893.2 \pm 22.1

concentrations compared to the other origins. However, the larger mean recorded for Local conditions might indicate the influence of meteorological factors and a certain loading of the atmosphere with methane of mainly anthropogenic origin, particularly related to the city of Valladolid, sporadic fugitive emissions from a nearby landfill, both in the S and SE wind sectors, and livestock in the region.

The background concentration established for the measuring site selecting the data without considering those associated with south and east wind sectors and stagnant conditions, among others, was 1892 ppb. The procedure provided representative baseline conditions, and controlling factors need to be borne in mind if a better understanding of CH₄ levels at other similar sites, particularly in southern Europe, is to be gained. More research should be carried out to identify and implement measures or aimed at changing techniques so as to achieve reductions in greenhouse gases.

Conflict of interest

The authors declare that there is no conflict of interest regarding publication of this paper.

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