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CO_2 AND CH_4 URBAN PLUME OVER A MEDITERRANEAN SEMI-NATURAL SITE IN THE IBERIAN PENINSULA

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ABSTRACT

CO_2 and CH_4 emissions are the two most significant greenhouse gas emissions in Spain. The current study analyzed the influence of a city urban plume over the final CO_2 and CH_4 mixing ratio values recorded at the Low Atmosphere Research Centre (CIB station), in the North of Spain. The measuring campaign lasted five and a half years, from 15th October 2010. CO_2 and CH_4 transport was analyzed through mixing ratio data obtained with a Picarro G1301 analyzer, which is based on cavity ring-down spectroscopy. Wind direction data were obtained at 2-m height. 16-wind direction sectors were considered. CO_2 and CH_4 detrended mixing ratios above the 90th percentiles were then calculated for each wind sector. Greater values in the southern sectors highlighted the influence of the nearby city of Valladolid, located approximately 24 km southeast. Faster growth in the southern sectors was found, since around 2.51 ppm year^{-1} (CO_2) and 9.33 ppb year^{-1} (CH_4) were obtained compared to 2.36 ppm year^{-1} (CO_2) and 9.03 ppb year^{-1} (CH_4) for the remaining sectors. Finally, 96-h backward air trajectories prior to reaching the CIB station were obtained with the METEX model at 500-m height a.g.l. Results showed a prevailing Atlantic origin of the masses, which finally impacted on the southern sectors, dragging pollutants from this area. The importance of the methodology used here lies in its easy and plausible application for other gases.
Keywords: plume, wind direction, backward air trajectories, METEX, detrended mixing ratios.

1 INTRODUCTION

Atmospheric back trajectories and transport models have been extensively used to identify potential emission sources at receptor locations by combining mixing ratio measurements with back trajectory analysis [1]. Back trajectories obtained using air models reveal the movement of an air parcel reaching the receptor point, where mixing ratios were measured. Thus, the pollutant origin could be inferred [2]. The atmospheric transport paths and the origin regions were established by means of back trajectory analysis and source-receptor methodologies, which determine the relationship between a receptor point and the probable source areas [1], [3].

Software programs for air trajectory calculation are frequently used to study the airflow pattern and source–receptor relation [4]. As Isakar et al. [5] stated, different modelling tools have been developed over the years to gain insight regarding the mobility of particles in the atmosphere. Some authors have employed the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, such as Adame et al. [6], who used forward trajectories to study the volcanic plumes' dispersion affecting Spain. Donnelly et al. [2], also employed HYSPLIT to determine the air mass path and identify the effects of regional air mass movement on air quality in Kilkitt (Ireland). Another potential web-based model to calculate the back trajectories is the METereological Data EXplorer (METEX) model, which was the model employed here due to its flexibility and ease-of-use [4].

According to Pérez et al. [7], extensive measuring campaigns have been conducted in recent years looking into learning details about CO_2 [8,9] and CH_4 evolution [10]. However, on a global scale, in situ CO_2 and CH_4 monitoring stations are still very limited outside major

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nations [11], [12]. Furthermore, analyzing the impact of urban plumes on rural environments is uncommon [7], [13].

The aim of the current paper is to analyze the urban plume, originated in the city of Valladolid, to gain a better understanding of the spatiotemporal impact of the urban sources arriving at the CIB station. The study area is located in the upper Spanish plateau, 24 km NW of Valladolid which is one of the most populous areas in the northwest sector of Spain with nearly 300,000 inhabitants [14]. A noticeable feature related to the dataset used is its length, which spans five and a half years of collecting measurements with scant gaps. This period could be considered sufficient to capture an urban plume when it is dragged by the wind, as Pérez et al. [7] stated.

The paper is organized as follows: Section 2 describes the study area and dataset, as well as provides a brief description of the METEX model. Section 3 presents the results in terms of CO_2 and CH_4 episodes and air mass modelling to infer the origin of the air masses. Finally, conclusions are detailed in Section 4.

2 MATERIAL AND METHODS

2.1 Study area

The sampling site is located at the Low Atmosphere Research Centre (CIB), 41°48′49″N, 4°55′59″ W, 24 km NW of Valladolid (Spain, 690 m a.s.l.). The location is a highly extensive plateau 845 m a.s.l, with no relief elements, thus ensuring horizontal homogeneity [13]. Agricultural crops, grassland, shrubland and isolated coniferous stands constitute the surrounding vegetation.

The climate across the sampling area is labelled as Mediterranean [15], with cold winters and warm-to-hot summers. Mean temperatures of 2.7ºC in January and 20.2ºC in July and mean annual precipitation around 450 mm are typical at the station [16].

2.2 Data

Data were collected in the period from 15th October 2010 to 29th February 2016. CO_2 and CH_4 mixing ratio values were obtained with the automatic PICARRO analyzer (G1301) based on cavity ring-down spectroscopy. The analyzer controls external solenoid valves to measure at three height levels: 1.8, 3.7 and 8.3 m. Only the highest level was considered in the current paper. Measurements extended over 10 min at each level and the first 20 data points were not considered with the aim of guaranteeing the quality of the calculated semi-hourly data when the solenoid valve level changes. Approximately 28 measurements per minute were collected and were then averaged to obtain semi-hourly mixing ratios [7]. In addition, the PICARRO was calibrated every two weeks with three NOAA standards to slightly correct the mixing ratio values recorded with the analyzer [7]. This quality protocol guarantees the quality of the data.

First CO_2 and CH_4 mixing ratio values were detrended by applying simple linear regression equations (mixing ratio vs time). Surface wind direction data were also considered to sort CO_2 and CH_4 detrended mixing ratio values into 16 wind sectors in order to identify the arrival trajectory direction. Surface wind direction data were obtained from the website service SIAR [17]. Data were obtained at the Medina de Rioseco meteorological station which is just 14 km NW from the monitoring station. In addition, wind directions at 500 m height a.g.l. were computed with the METEX model. 90th percentile values were then calculated within each wind direction sector enabling the identification of locally-occurring episodes, in line with Domínguez-López et al. [18] methodology.

2.3 METEX model description

Plume transport simulations were obtained with the METereological data EXplorer (METEX) model [19] over the period of 15th October 2010 to 29th February 2016. A kinematic model on the NCEP reanalysis with 96-h back trajectory, with segment end points of 60-min and 500 m height a.g.l., was computed to analyze the origin of the air mass, linking its origin with low or high mixing ratio values, as also did Donnelly et al. [2]. Kinematic back trajectories consider that an air parcel is given by the horizontal wind component and vertical pressure velocity [20]. NCEP analysis was used as meteorological input files. This series uses the data with a temporal resolution of 3 hours and spatial resolution of 0.5ºx0.5º in latitude and longitude on pressure levels between 1 hPa and 1000 hPa.

CO_2 and CH_4 mixing ratio values were then studied by taking into account the trajectories' origin in order to estimate potential source regions and classify the trajectories as urban or rural influent sectors.

3 RESULTS AND DISCUSSION

3.1 CO_2 and CH_4 episodes determination

In order to assess the influence of the southern sectors on the final CO_2 and CH_4 mixing ratio values recorded by the PICARRO analyzer (G1301), mixing ratios were first detrended by simple linear regressions. 90th percentile values were then calculated within each of the 16 surface wind direction sectors established. 90th percentile values were calculated since higher levels are considered outliers, i.e. episodes. A similar methodology was employed by Domínguez-López et al. [18], although they considered episodes values as above the 95th percentile.

90th percentile values for our dataset are depicted in Fig. 1, revealing higher detrended mixing ratios for the southern sectors in both CO_2 (Fig. 1(a)) and CH_4 results (Fig. 1(b)), which means that the CIB station is influenced by local/regional sources. From here, the southern sectors will be labeled as urban sectors, since the Valladolid plume could be noticed, and the remaining sectors will be labeled as rural sectors since no important sources were found.

CO_2 influence sectors were found for the ESE, SE and SSE sectors. A mean value of 17 ppm for the southern sectors was found, whereas a mean value of around 9 ppm was found for the rural sectors. With regards to CH_4, the urban sectors were found for the SE and SSE sectors, showing around 90 ppb versus the 33 ppb calculated for the rural sectors. These results evidenced the influence of the southern sectors on both gases, thus enabling the Valladolid plume effects to be captured in the final mixing ratio measured at the CIB station. Furthermore, these results are in line with those found by Pérez et al. [13] which reported mixing ratio median values 8 ppm higher in the Valladolid sector compared to the rest of sectors.

3.2 Directional analysis

According to Pérez et al. [21], histograms are easy tools to describe data patterns. In order to investigate the influence of southern sectors, a 16-surface wind direction sector histogram was depicted in Fig. 2.

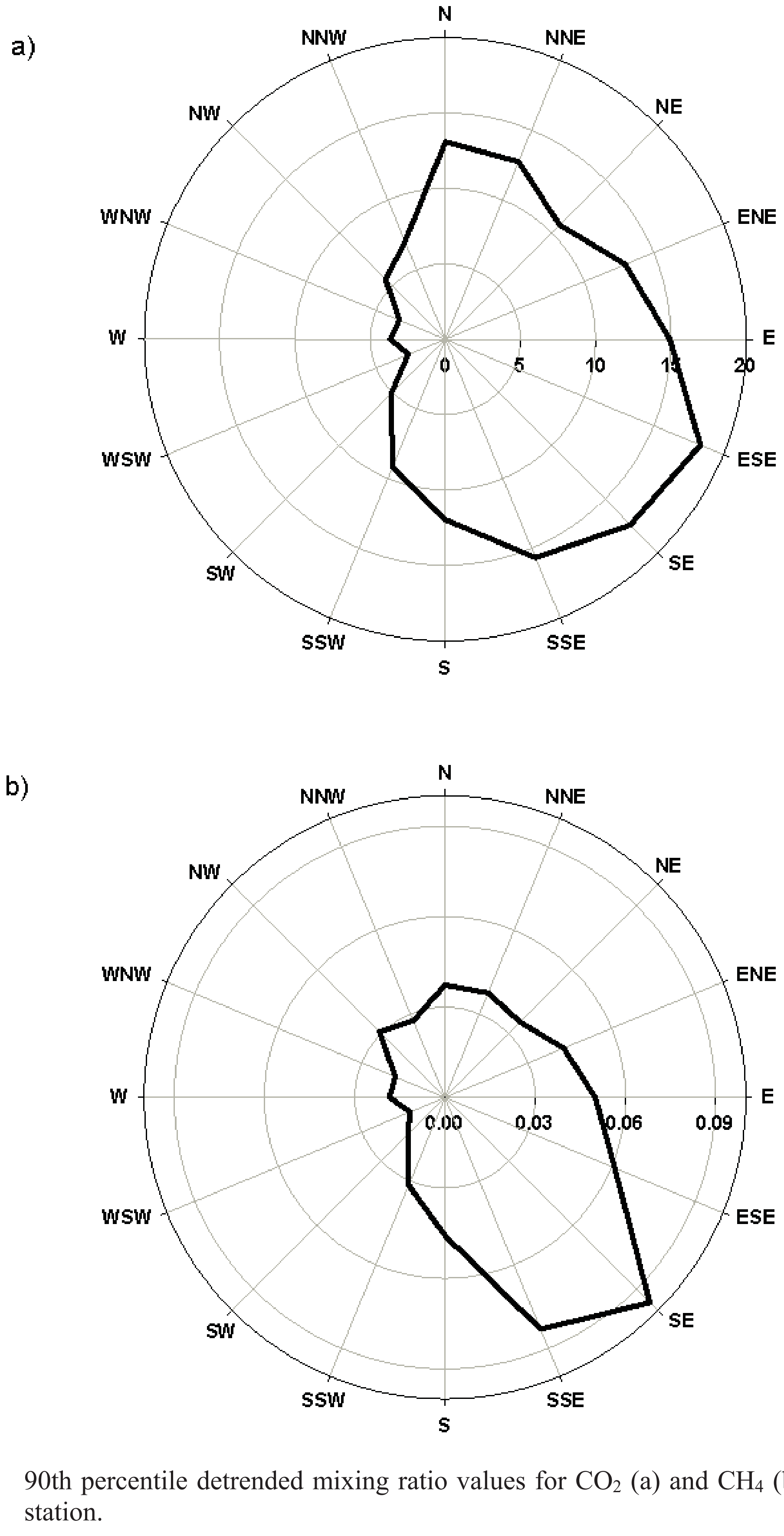

Figure 1: 90th percentile detrended mixing ratio values for CO_2 (a) and CH_4 (b) at CIB station.

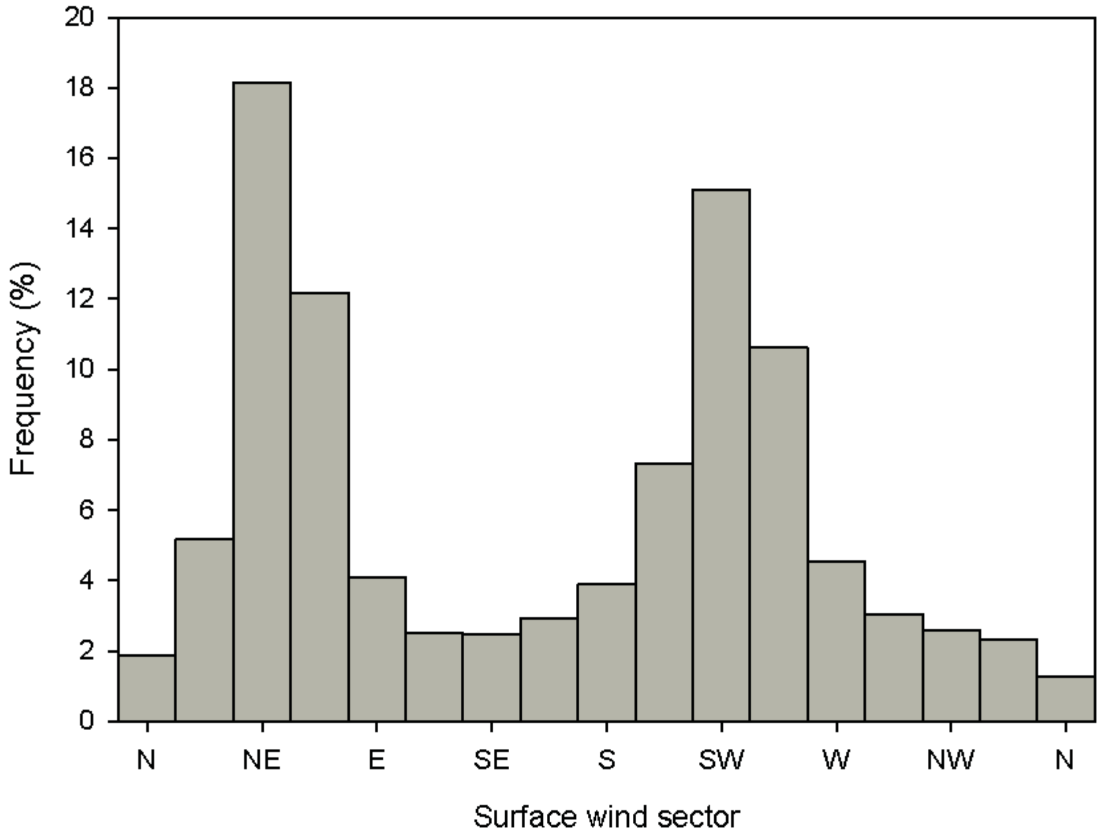

Figure 2: Frequency distribution of surface wind direction for mixing ratio values above the 90th percentile.

Fig. 2 shows two peaks associated with frequent surface wind direction surrounded by a wider sector where these observations proved much less frequent. The first peak was located at around 60º, linked to Palencia city, and the second one located at 220º. Both peaks correspond with the prevailing wind direction at the sampling area. Thus, over this direction, mixing ratios were lower due to the pollutant dispersion. According to Pérez et al. [13], the distribution shape for the Palencia sector should be similar to the rural sector since the plume dilution is high. The Palencia plume could only occasionally have a more direct impact on the measuring point.

3.3 Plume dispersion

Once directions associated with high mixing ratios were established, back trajectories were calculated with the METEX model to gain an overview of the features of long-range transport. According to Donnelly et al. [2], the choice of trajectory duration is crucial because too short of a duration may miss the emission sources and important air mass route crossings while too long of a duration could introduce noise (uncertainty) into the analysis and produce misleading results. Other authors, such as Isakar et al. [5], consider that a week may be too long for integration time, suggesting shorter exposition times to obtain more detailed conclusions, especially regarding anthropogenic activities near the sampling site. Thus, hourly plume dispersion during 96-h were finally tracked covering air mass movement in the Iberian Peninsula and surrounding areas. Furthermore, Domínguez-López et al. [18]

considered this trajectory duration enough to represent the synoptic air flow.

Due to the small NCEP files resolution, Domínguez-López et al. [18] do not recommended calculating back trajectories at lower atmospheric levels than 500 m a.g.l. Therefore, back trajectories were computed at 500 m a.g.l. in the current study.

Back trajectories for urban and rural sectors were computed separately. The pathway drawn by the mean back trajectories allow for a more refined interpretation of the air mass arrival to the study area [1]. Fig. 3 depicts the 96-h back trajectories calculated with METEX model at 500 m a.g.l.

The geographical distribution of mean back trajectories originating at the CIB station depicted in Fig. 3 shows a clear path from the west, reaching the Iberian Peninsula, mainly dominated by the atmospheric general Atlantic regime circulation [6], [22]. However, differences between the rural and the urban mean trajectories could be inferred from Fig. 3. On the one hand, the rural mean back trajectory travelling from the western part of the Iberian Peninsula and reaching the CIB station after crossing the northern area of the peninsula (blue line) could be observed. The same airflow was described by Izquierdo et al. [1]. The effect of the orography on the atmospheric transport patterns was noticeable, as pointed out by Izquierdo et al. [1], since the Cantabrian range appears to act as a barrier to the transport and dispersion of air masses arriving at the measuring point from the rural sectors. According to Notario et al. [22] trajectories coming from the North are frequent in the Iberian Peninsula. On the other hand, mean back trajectory associated with the southern sectors (red line) came

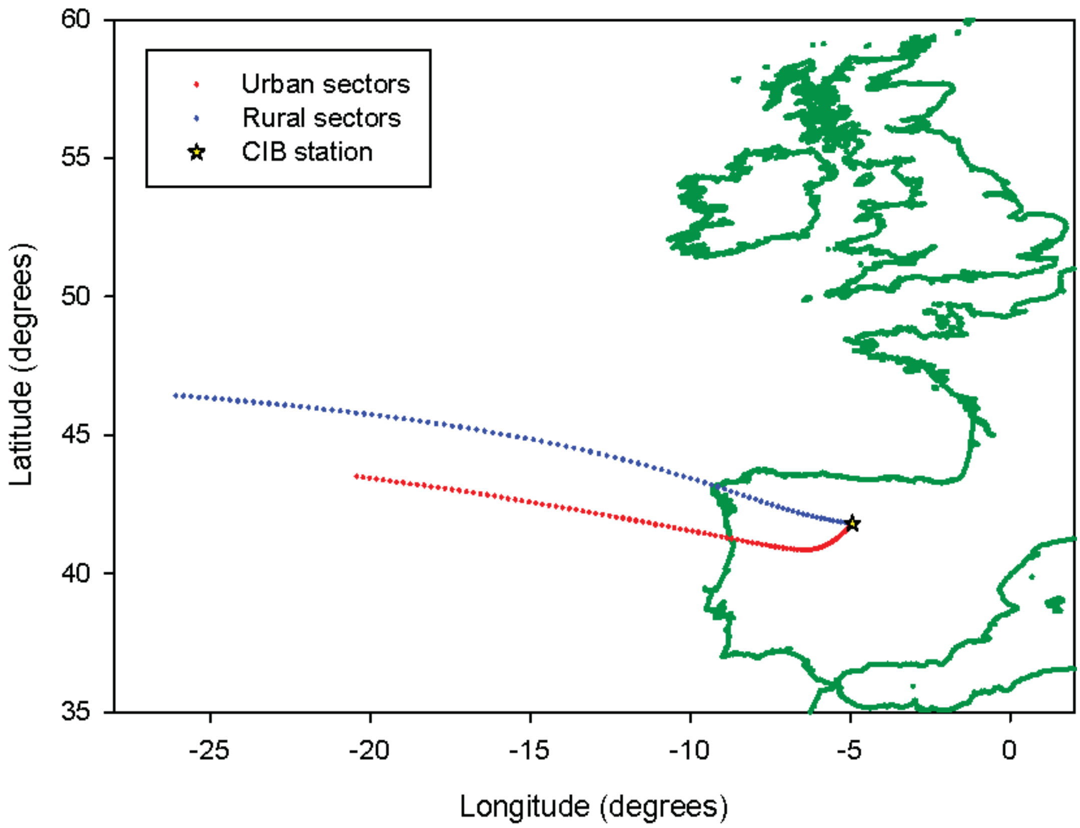

Figure 3: Plume origin 96-h before hitting CIB station. The red line represents the air mass arrival from the southern sectors. The blue line depicts the origin of the air mass involving the rural sectors before hitting the CIB station.

also from the Atlantic, following the general wind regime, but the last day before arriving at CIB the mean back trajectory changed direction toward the southwestern sectors. It should be noted that back trajectories were computed at 500 m height a.g.l., so the path flow is distorted due to the Ekman spiral effect. As height increased, a clockwise turning is evident, reaching approximately 30º at 300 m height a.g.l. according to Pérez et al. [21] results. Thus, taking into account this deviation, last 24-h computed from the southern sectors has a southwestern origin, which may be influenced by the Valladolid plume.

Other important differences could be observed between rural and urban mean back trajectories shown in Fig. 3. First, rural mean back trajectory requires more time and greater distance travelled to arrive at CIB, so the pollutant mixing ratio is diluted along its path. According to García et al. [23], Atlantic air masses are defined as "clean trajectories" since they drag low pollutant mixing ratios. In contrast, urban mean back trajectory impacted the Iberian Peninsula faster and travelled shorter distances [13], which implied a greater drag of pollutants, due to a lower pollutant dilution factor. Moreover, an important recirculation was noticeable in the urban mean back trajectory for the last 24-h (Fig. 3). As García et al. [23] stated, local trajectories (trajectories confined within the Peninsula) are normally characterized by higher pollutant concentrations which explain the greater mixing ratio values found for both gases in the southern sectors.

Table 1 presents growth rate and the initial mixing ratio values over the study period for CO_2 and CH_4. Higher initial mixing ratio values for both gases were linked with trajectories coming from the urban sectors due to the transport caused by continental air masses. The transport from the southern sectors which are more industrialized combined with the recirculation noticed in Fig. 3 explain the higher initial mixing ratio and growth rate values of the southern sectors. As stated by Pérez et al. [13], the Valladolid plume retains source features. The highest mixing ratios obtained in the Valladolid sector were partially a result of the strength of the source. On the contrary, CO_2 and CH_4 initial mixing ratio values were lower concerning the rest of sectors since air masses tend to arrive via marine from the North Atlantic Ocean. The same behavior was found by Isakar et al. [5].

4 CONCLUSIONS

CO_2 and CH_4 Valladolid plume transport were analyzed over five and a half years of mixing ratios measurements obtained at 8.3 m a.g.l. with a PICARRO analyzer (G1301) at CIB station. CIB is affected by both local and long-range transport pollution. Mixing ratios were detrended, and in order to consider only high concentrations, the 90th percentile values were calculated within each 16-wind sector. Back trajectories were used to determine the atmospheric pathways of the air masses reaching the station during the study period. Two different sectors were then considered: urban sectors, which were related to the southern sectors in which Valladolid is located and the rest of the sectors which were labeled as rural sectors. Mean rural and urban 96-h back trajectories at 500 m height a.g.l. were computed

Table 1: Growth rate and initial mixing ratio values for the rural and urban sectors at CIB station.

	CO_2		CH_4	
	Growth rate (ppm year^{-1})	Initial mixing ratio (ppm)	Growth rate (ppb year^{-1})	Initial mixing ratio (ppb)
Rural sectors	2.36	395.72	9.03	1883.59
Urban sectors	2.49	400.31	9.33	1914.47

with the METEX model separately. Back trajectory analysis clearly revealed two different pathways prior to reaching the CIB station: from the west travelling through the Atlantic Ocean and entering by the North of the Iberian Peninsula (rural sectors), and from the west travelling through the Atlantic Ocean but finally entering the southwestern part of the peninsula with a noticeable recirculation (urban sectors). These results support the argument that southern sectors drag pollutants to the sampling area, increasing their mixing ratio values. Moreover, urban back trajectories' paths were shorter than rural back trajectories' paths, leading to lower dispersion processes and thereby higher CO_2 and CH_4 mixing ratio values in urban sectors. Furthermore, the shorter time required by the Valladolid plume to reach the CIB station, should not be ignored since it implies a lower mixing in the atmosphere. The highest mixing ratios obtained in the Valladolid sector were partially a result of the strength of the source. Finally, growth rate values increased more rapidly for the southern sectors, as well as the initial mixing ratio values which were greater for the southern sectors, showing the Valladolid urban plume at the monitoring station.

In conclusion, this paper provides a first assessment of the possible influence of the southern sectors on final CO_2 and CH_4 mixing ratios measured at the CIB station. However, further studies are needed to confirm these results.

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