Daily carbon surface fluxes in the West Ebre (Ebro) watershed from aircraft profiling on late June 2007

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(Manuscript received 23 October 2009; in final form 11 June 2010)

ABSTRACT

An intensive aircraft campaign measuring atmospheric CO₂ mixing ratios was carried out in the central part of the Ebre watershed on late June 2007 to characterize the CO₂ dynamics in the Ebre basin and to calculate the regional cumulative carbon surface flux. CO₂ concentrations were obtained from vertical profiles over La Mucla (LMU; 41.60°N, 1.1°W) from 900 to 4000 m above the sea level (masl), horizontal transects at ~2000 m 100 km west from LMU, and continuous measurements at ~650 masl. Different estimates of surface flux from changes in the convective boundary layer (CBL) CO₂ concentration were obtained following the Integral CBL budgeting equation (ICBL) and the carbon content integration (CCI) method. Values of the mean surface flux calculated from the different approaches range from –2.4 to –7.9 μmolCO₂/m²s. Regional surface flux calculated from vertical profiling appears to be consistent in a distance of 70 km away from the measurement site. The ICBL method is very sensitive to the accurate determination of the concentration in the entrainment zone. The overall uncertainty from fluxes calculated from the ICBL method rises to a value of 70%, whereas the uncertainty linked to the CCI method is 55%.

1. Introduction

Knowledge of sources and sinks of atmospheric carbon dioxide is crucial for understanding the partitioning of anthropogenic fluxes in a climate change context (Raupach et al., 2007). Great efforts have been focused towards understanding the distribution of the atmospheric CO₂ uptake by land and ocean on a global/continental scale (e.g. Tans et al., 1990; Ciais et al., 1995; Fan et al., 1998; Peters et al., 2007). Eddy-covariance flux measurements provide measurements of local ecosystem carbon balances on spatial scales of a few hundreds of metres (Wofsy et al., 1993; Baldocchi et al., 1996; Valentini et al., 2000). However, the distribution at the regional scale is still uncertain. Information about regional scale biosphere–atmosphere exchange can be extracted from mixing ratios of CO₂ over the continent, close to the terrestrial biospheric activity (Gerbig et al., 2006). Regional carbon fluxes estimated from available atmospheric CO₂ measurements contribute to understanding the dynamics of the carbon uptake/release over continental areas. Long-term observations of CO₂ within the continental atmospheric boundary layer (ABL) with significant accuracy available from tall towers (Bakwin et al., 1998), eddy flux towers (Wofsy and Harris, 2002) and aircraft measurements (Lloyd et al., 2001) appear closer to the regional fluxes of CO₂, specially when compared to observations from above the ABL or from remote stations at the same latitude (Gerbig et al., 2006). Carbon sinks and sources distributions and their seasonal variability obtained from field measurements on different ecosystems are needed to establish a numerical global model of CO₂ concentrations (Yamamoto et al., 1996).

During good weather conditions, daytime convective boundary layer (CBL) is clearly distinguishable; the air layer is vertically confined and it grows during the day at a predictable rate by incorporating portions of overlying air. In addition, the bulk physical properties and the composition of the CBL are independent of small-scale surface heterogeneities acting as a natural mixing chamber for surface fluxes over heterogeneous terrain. An estimate of the average gas flux at the surface over which a column of air has travelled, can be made by following changes in the tracer gas concentration in the mixed layer and
the CBL height over the day and allowing for entrainment. As CBL budget is based on concentrations in the mixed layer, they represent regionally averaged surface fluxes for the landscape along the trajectory of the mean wind the air column is moving. Usually, calculated fluxes are representative of an average area of 10^3–10^5 km^2, which extends about 100 km upward (Denmead et al., 1996).

Previous studies highlighted the appropriateness of air-borne data to derive information about the underlying carbon surface fluxes (e.g. Gerbig et al., 2003a; Crevoisier et al., 2006; Lloyd et al., 2007; Stephens et al., 2007; Font et al., 2008). The application of CBL techniques using aircraft data have been conducted in different regions and times. Martins et al. (2009) performed a Lagrangian experiment over a homogenous landscape of agricultural land-use in Iowa, USA (41°44’N 92°96’W) on June 2007 and they estimated a net CO2 surface flux of −9.0 ± 2.4 μmolCO2/m^2s. The CO2 budget schema applied to aircraft observations during the CERES campaign (CarboEurope Regional Experiment Strategy) (Dolman et al., 2006) calculates a mean surface flux ranging from −16.8 to −8.6 μmolCO2/m^2s in Les Landes region (SW France), characterized by a landscape mixture of maritime pines and agricultural lands, on June 2005 (Sarrat et al., 2009).

In this study, the net regional surface flux is estimated from available vertical profiles of CO2 mixing ratios measured at La Muela site, in Spain (LMU; 41.60°N 1.1°W) applying two different CBL budget methods (Section 2). First, the integration convective boundary layer (ICBL) is applied taking into account changes in the carbon content and the convective dynamics (Section 3.2.1). The role of the entrainment flux is addressed in Section 3.2.2. Secondly, the carbon content integration (CCI) method is applied, to account for turbulent fluxes at different heights. A fitting equation is proposed to extrapolate the flux at the surface level (Section 3.2.3). The robustness of the two methods and the sources of uncertainty are later discussed (Section 4). As a final result, a preliminary estimation of the annual carbon cycle in the Ebre watershed is presented.

2. Methods

2.1. The ICBL budget method
This method is applicable in sunny days under fine weather conditions when the atmospheric pressure is high and the bulk of the troposphere consists of dry, slowly subsiding air (Raupach et al., 1992). The height of the CBL grows during the day as thermal plumes overshoot the capping inversion and entrain overlying air into the CBL. A mass balance shows that the rate of change of the CO2 concentration in the CBL is a function of the growth rate of the CBL, the vertical velocity at the top of the CBL, the CO2 concentration of air being entrained and the surface flux (Raupach et al., 1992; Denmead et al., 1996; Lloyd et al. 2001; Styles et al., 2002; Wang et al. 2007):

\[
\frac{\partial s_m}{\partial t} = \frac{F_i}{\rho_m h} + \left( \frac{s_s - s_m}{h} \right) \left( \frac{\partial h}{\partial t} - W_s \right) \frac{\rho_s}{\rho_m},
\]

where \(s_m\) is the mean CO2 concentration in a column of air extending from height \(z = 0\) to \(z = h\) and moving with the mean wind field, \(s_s\) is the concentration just above the top of the CBL, that is, the concentration of the air entrained into the CBL while it grows; \(F_i\) is the sum of all fluxes at the surface, \(\rho_m\) and \(\rho_s\) are the molar air density within the CBL and at the top of the CBL height, respectively and \(W_s\) is the mean vertical velocity at the top of the CBL, defined as positive upwards. The first term of the right-hand side of eq. (1) accounts for the effects of the surface flux on mixed layer concentration; and the second, the effects of entrainment and vertical motion.

Reorganizing eq. (1), the surface flux can be derived and written as

\[
F_i = \rho_m h \frac{\partial s_m}{\partial t} - (s_s - s_m) \rho_s \left( \frac{\partial h}{\partial t} - W_s \right) + W_s \rho_s (s_s - s_m).
\]

This is the basis of a differential form of the CBL budget method (Raupach et al., 1992). Eq. (2) yields the regionally averaged flux over the along-wind trajectory of the CBL air column. Traditionally, the first term is called the storage flux (Wang et al., 2007); and the sum of the last two terms on the right-hand side of eq. (2) is called the entrainment flux (Garratt, 1992; Wang et al., 2007). Four assumptions are made: (a) the boundary layer is well mixed above the surface layer; (b) the effects of the horizontal advection are neglected; (c) the transition layer between the CBL and the free troposphere (FT) above, also called the entrainment zone (EZ) is assumed to be thin compared with the ABL height, which is likely in a region under the influence of high-pressure system with strong subsidence (Wang et al., 2007). In the EZ, FT air is incorporated into the CBL, causing its increase during the day (Stull, 2000) and (d) the concentration above the boundary layer, \(s_s\), is constant in time.

The integral CBL budget equation (ICBL) is obtained by integrating eq. (2), this process giving the average surface flux over a period (3)

\[
I_s = \frac{(s_{m(t)} - s_s) \rho_{m(t)} h_{t2} - (s_{m(t)} - s_s) \rho_{m(t)} h_{t1}}{\Delta t} - (s_m - s_s) W_s \langle \rho_s \rangle,
\]

where angle brackets denote time averaging and \(\Delta t\) is the integration period from \(t_1\) to \(t_2\). The average of the product of quantities in the subsidence term is approximated by the product of their averages (Styles et al., 2002).

Eq. (3) yields cumulative surface fluxes representing the area traversed by a column of air in the course of the integration period. The streamwise and lateral length scales are given by \(u(t_2-t_1)\) and \(\sigma_u(t_2-t_1)\) respectively, with an averaging area of \(u(t_2-t_1)^2\), where \(u\) is the mean horizontal wind speed in the CBL and \(\sigma_u\) is the standard deviation in the lateral velocity (Levy et al., 1999).
2.2. Entrainment flux

When $W_2$ is non-zero at the top of the boundary layer and the CO$_2$ concentration within the layer differs from that in the free troposphere, a CO$_2$ flux into or out of the column must be accounted, or the mass within the column is not conserved (Martins et al., 2009). Then, the entrainment flux or subsidence is accounted by

$$F_e = (s_m - (s_i))W_4 \rho_i. \tag{4}$$

Brackets indicate time-average values. A negative $F_e$ denotes entrainment from the free troposphere to the boundary layer (subidence).

The ratio of the entrainment flux related to the surface flux denotes the importance of the entrainment processes

$$\beta = F_e/I_s. \tag{5}$$

de Arellano et al. (2004) first estimated the order of magnitude of the $\beta$-ratio for carbon dioxide. When $\beta > 1$, the dilution processes due to the entrainment of the FT air masses dominate; for $0 < \beta < 1$, the ventilation process is still relevant, but the uptake by vegetation progressively becomes dominant; whenever $\beta < 0$, the surface flux is predominant.

2.3. Carbon content integration method

The CCI method, also called the height integration method, defines a fixed integration height to estimate the mean surface flux (Wofsy et al., 1988; Chou et al., 2002; Styles et al., 2002 Martins et al., 2009). The surface flux that crosses a surface can be calculated as

$$I_s = \frac{\rho_0s_{i2}\sigma_{12}H_i - \rho_0s_{01}\sigma_{01}H_i}{\Delta t}, \tag{6}$$

where $s_{i2}(i)$ is the mean CO$_2$ concentration for the altitude bin $i$ above the layer considered for the profile sampled at $t_2$; and $s_{01}(i)$ is the mean CO$_2$ concentration for the same altitude bin for the first profile sampled at $t_1$; $H_i$ is the width of the layers considered; $\rho_0$ is the molar air density at the height-$i$ and $\Delta t$ is the integration period elapsed between the two samplings. Knowing all the fluxes crossing the $i$-layers, a function of the surface flux propagation in altitude is adjusted, further allowing the extrapolation of the flux at the surface layer ($I_s$).

The fitted equation of the turbulent fluxes in altitude is related to the vertical gradient of CO$_2$ concentration. Under clear convective conditions, buoyancy is the dominant mechanism driving turbulence. Except near the surface, conserved variables such as potential temperature or CO$_2$ are almost constant with height due to the strong mixing. In such quasi-steady situations, turbulent fluxes follow a linear profile with height (Stull, 1988; Casso-Torrallba et al., 2008). But in those situations where the carbon gradient in altitude follows an exponential fit, the turbulent fluxes also follow an exponential decay in altitude.

3. Results

3.1. CO$_2$ mixing ratios in the Ebre watershed

Vertical profiles of atmospheric CO$_2$ mixing ratios were sampled on 26 and 27 June 2007 within the ICARO-2 (Reduction of Uncertainties in the peninsular CARbon balance by means of Oscillating tropospheric transects) project in Spain at La Muela (LMU), NE Spain, within the central part of the Ebre watershed basin. Topographically, the central region of the Ebre basin is flat, with an average altitude of 250 masl. Vegetation in the region is characterized by complex agricultural patches, dominated by permanent crops and non-irrigated lands except for those situated along the irrigated channels derived from the Ebre River, where intensive irrigated arable lands persist. The dominant permanent crops comprise vineyards and olive groves. In the intensive irrigated areas along the irrigated canals, extensive herbaceous crops dominate (alfalfa, maize, cereals, etc.) and fruit growing and horticulture shape the land. The Moncayo mountain range is situated 100 km west of LMU, and natural forests of holm oak and kermes oak dominate the lowest levels of the mountain range, while oaks, beechwood and birch dominate the highest and wetter regions. The Pyrenees mountain range is 150 km north of the site and is covered by alpine forests.

The campaign was undertaken during the Northern Hemisphere growing season. Local vegetation was fairly active as indicated by the NDVI 10-day composition map (Fig. 1a). Vegetation around LMU was photosynthetically not very active (values ~0.2) except for the one situated along the irrigation channels, reaching NDVI values of ~0.5. The average NDVI value for the region situated around LMU (~60 km) during the campaign was 0.41, slightly above the annual mean NDVI value (0.36). For 2007, the vegetation in the region was more active photosynthetically during late April and early May, with NDVI values that reached 0.55 as seen in Fig. 1(b). On late June, vegetation was still above the annual mean value (0.37) but the photosynthetic activity started decreasing. The time when vegetation was less active was registered in mid-September and December (~0.27). The 1998–2006 time series of the fPAR index (Gobron et al., 2006) at LMU (Fig. 1c) shows that April and May are the most active months in LMU, with a decreasing activity in June. Generally, July and August are the most inactive seasons linked to the dry weather conditions occurring during summer time in the central part of the Ebre watershed. Regarding the synoptic weather situation, the field campaign was carried out under fairly anticyclonic conditions with light NW surface winds (~4–5 ms$^{-1}$) that prevailed during the daytime in the central part of the Ebre watershed.

Vertical profiles of atmospheric CO$_2$ mixing ratios were sampled with the portable non-dispersive infrared instrument developed by AOS Inc. The mean precision of the system in laboratory conditions is ±0.11 ppmv whereas under flight conditions the mean precision is estimated at $\sigma \pm 0.23$ ppmv. Further details
Fig. 1. (a) Ten-day composition NDVI map starting on 21 June 2007 from SPOT10 products (http://www.vgt.vito.be). Black dot shows the LMU site. (b) 2007-LMU-NDVI time series. The red dot shows the NDVI value for the period when the survey was done; dotted line marks the annual NDVI mean. (c) 2000–2006 LMU-IPAR time series (EC-JRC-2010; http://fapar.jrc.ec.europa.eu/). Red curve denotes the mean seasonal behaviour of IPAR through years. Blue line denotes the average IPAR value for the time encompassed.

about the instrumentation may be found in Font et al. (2008). Four vertical profiles were sampled at different times during the survey (Fig. 2a). The first profile sampled on 26 June started around 8 UT, from now on abridged P1. CO₂ mixing ratios at the lowest levels were \(\sim 386\) ppmv, decreasing in height and reaching \(\sim 384\) ppmv at 2000 masl. Conversely, the profile sampled later in the day (starting at 17.50 UT, P2) shows quasi-homogeneous concentrations in height, with values \(\sim 382\) ppmv until 2000 masl, and tending to slightly increase up to 2500 masl. The profiles on 27 June 2007 were sampled around noon, starting 30 min apart. They comprised the entire air column over LMU from 1000 to 4000 masl. Ascent and descent profiles are referred as P3 and P4, respectively. The lowermost part of P3 and P4 beared strong similarities, with concentrations ranging from \(\sim 386\) ppmv at \(\sim 1000\) masl down to \(\sim 383\) ppmv at 2000 masl. From 2000 to 4500 masl, large variations and discrepancies between P3 and P4 appeared. Between 2000 and 3000 masl, a rich CO₂-mixing ratio layer was detected in P3 (\(\sim 384\) ppmv), while P4 registered quasi-homogeneous values (\(\sim 382\) ppmv). Between 3000 and 3500 masl, P3 measured lower CO₂ concentrations (\(\sim 381.5\) ppmv). Instead, P4 sampled a rich-CO₂-content layer (\(\sim 384\) ppmv). From P3 and P4 profiles it is stated that CO₂
Fig. 2. CO₂ measurements at LMU (NE Spain) during 26 and 27 June 2007. (a) Vertical profiles (circles) and the mean CO₂ concentration from the tall tower site recorded from the three available altitudes during the aircraft survey (squares); altitude of the convective boundary layer extracted from NCEP-GFS meteorological model, interpolated at the time of the flight (dotted lines); and schematic representation of the mixing rations applied in eq. (3) and summarized in Table 1. ASC refers to the ascent profile; DES, to the descent one. (b) Continuous CO₂ measurements at LMU tower on 26 and 27 June 2007. Coloured rectangles show CO₂ measurements when profiles were sampled.
changes within the lowermost part of profiles are slower than the ones occurring higher in the altitude.

An 80-m-height tower situated in a plateau at 570 msl in the middle of the Ebre basin at LMU (250 msl) is equipped with a LiCor-7000, providing a continuous measuring of atmospheric CO₂ mixing ratios at three different altitudes [41, 57 and 79 m above the ground level (magl)]. A target gas is measured every 200 min to control drifts. Whenever the mean precision is above 0.05 ppmv the instrument is restarted and re-calibrated (Morguí J.-A., 2008, personal communication). Hourly means at 41 and 79 m are shown in Fig. 2(b). Coloured rectangles mark CO₂ measurements exactly when profiles were carried out. Continuous measurements showed a marked diurnal cycle, with high atmospheric CO₂ values during night and low values during central hours of the day. The diurnal amplitude (maximum minus minimum CO₂ concentrations) was ∼5.25 ppmv on 26 June, whereas it was larger on 27 June, of around ∼8 ppmv. The maximum concentration was registered between 2 and 3 UT on 26 June; and between 5 and 6 UT on 27 June, with values of ∼386.4 and ∼386.7 ppmv, respectively. The minimum concentration on the 26 June took place between 17 and 20 hours (∼381.4 ppmv), whereas the minimum on the 27 June occurred between 21 and 23 h, with values of ∼379.0 ppmv. Ground concentrations were calculated at LMU at the time when profiles were sampled, taken as the weighted average concentration from the measurements at the three altitudes of the tower. At the time P1 was sampled, ground CO₂ concentration was 384.9 ppmv; 381.5 ppmv for P2 and 384.7 ppmv for P3. Measurements from the LMU tower are therefore consistent with those from the aircraft sampling (Fig. 2a) and provide a continuity of CO₂ measurements from the lowest aircraft altitude down to the surface.

Additionally to the vertical profiles and tall tower continuous measurements, horizontal transects at ∼2000 and ∼2500 msl were flown on 26 June, following the 41.60°N parallel, 100 km west from LMU at ∼8:00 and ∼17:30 UT (Fig. 3). The mean CO₂ concentrations (±1σ) of stacks were 383.33 ± 1.03 and 381.47 ± 0.62 ppmv, with a range difference of 4.45 and 3.11 ppmv, respectively. It is seen that there was a decrease of the mean CO₂ concentration in the horizontal legs of ∼2 ppmv between the two sampling times. The horizontal transect measured in the early morning on 26 June 2007 showed large CO₂ differences between regions. Large CO₂ mixing ratios were measured near LMU (∼385 ppmv) whereas further west, lower mixing ratios were registered (∼380 ppmv). The afternoon stack showed less variability. However, differences still showed up: close to LMU higher concentrations prevailed (∼382 ppmv) compared to the lower concentrations 100 km west (∼379 ppmv).

![Fig. 3. Aircraft measurements along a 100-m-track west from LMU at (a) ∼8:00 UT and (b) ∼18:00 UT on 26 June 2007. Black line denotes the topographic profile, extracted from GTOPO30 global digital elevation model (DEM) from the U.S. Geological Survey’s EROS Data Center in Sioux Falls, South Dakota; data and documentation available at http://edc.usgs.gov/](image-url)
Table 1. Parameters used to calculate CO2 fluxes at LMU by ICBL and CCI methods

| Time (UT)          | 26/6/2007 08:00 (P1) | 26/6/2007 17:55 (P2) |
|--------------------|----------------------|---------------------|
| $s_{m-a}$ (ppmv)   | 384.93 ± 0.81        | 382.05 ± 0.37       |
| $s_{m-a+1}$ (ppmv) | 385.10 ± 0.25        | 381.77 ± 0.40       |
| $s_a$ (ppmv)       | 382.36 ± 0.47        |                     |
| $s_N$ (ppmv)       | 384.05 ± 0.24        | –                   |
| $h_{CBL}$ (magl)   | 969 ± 7              | 1326 ± 277          |
| $\rho_m$ (molm⁻³) | 40.3                 | 39.1                |
| $W_a$ (ms⁻¹)       | −0.014               | −0.009              |

$s_{m-a}$ is the average CO2 concentration in the CBL taking into account only aircraft observations; $s_{m-a+1}$ indicates that both aircraft and tall tower measurements are used to calculate the CBL average concentration; $s_a$ is the CO2 concentration in the FT; $s_N$ is the concentration of the residual layer; $h_{CBL}$ is the height of the convective boundary layer, in metres above the ground level (magl); $\rho_m$ is the molar air density within the CBL; $W_a$ is the vertical velocity at the top of the CBL. The last three parameters are extracted from the NCEP-GFS model.

3.2. Carbon regional surface flux estimated from vertical mixing ratios profiles

The calculation of the mean carbon regional surface flux using ICBL and CCI methods from changes in the CO2 mixing ratios measured in vertical profiles during 26 June between the morning and afternoon profiles is possible as the campaign was done under anticyclonic weather conditions and the wind direction did not change in the interval when profiles were sampled (NW, with average velocity of 4–5 ms⁻¹).

3.2.1. Results from ICBL method. The parameters used to calculate the cumulative surface flux from the ICBL formulation are summarized in Table 1. The CBL height is extracted from NCEP-GFS meteorological global model (resolution $1° \times 1°$; 26 vertical layers; 6 h analysis; 3 h forecast) and linearly interpolated to the central time of the profiles. Due to the lack of radiosounding data for that period, no alternative method to estimate the CBL height is currently available. Molar air density in the CBL is calculated from vertical profiles of temperature, humidity and ambient pressure below the CBL from the NCEP-GFS data, as well as the vertical velocity and the molar density at the top of the CBL. The mean CBL CO2 mixing ratio from vertical profiles ($s_{m-a}$) is 384.93 ± 0.81 ppmv (P1) and 382.05 ± 0.37 ppmv (P2). The FT concentration ($s_a$) is expected to be representative of a large area and less influenced by the short-term variability of surface fluxes. Different studies have considered the maritime concentration measured at baseline monitoring stations as representative of $s_a$ (e.g. Denmead et al., 1996). The marine boundary layer (MBL) matrix provides latitudinal reference values (Masarie and Tans, 1995; GLOBALVIEW, 2008). However, 20 years of extensive aircraft data over the north Pacific presented a significant seasonal bias of up to 2 ppmv in the free troposphere compared to the MBL value, being therefore not always a suitable boundary condition (Gerbig et al., 2003b). For the Ebre field campaign, the MBL reference values were 382.75 ppmv (P1), 382.68 ppmv (P2) and 382.56 ppmv (P3 and P4). As an alternative, $s_a$ can be estimated from vertical profiling. In this study, we considered the profiles sampled on 27 June 2007, as P3 and P4 encompass the CO2 mixing ratios up to 4000 masl. To make sure that $s_a$ does not carry the upwind surface fluxes signal, residence time is calculated in the surface layer of air masses, 48 h before arriving at the sampling site. To this end, the Lagrangian Particle Dispersion Model FLEXPART is used in backward mode (Stohl et al., 2005). At 3750 m, air masses have no surface influence 48 h before the sampling took place (Fig. 4). As a result, CO2 mixing ratios measured at this altitude are considered as representative of the FT concentration, this resulting into a concentration of 382.36 ± 0.47 ppmv. If we compare the two reference values, the MBL concentration is at most, only 0.39 ppmv larger than that estimated from in situ profiles. Eventually, $s_a$ is taken from the aircraft data as being a much better representation of the boundary conditions for LMU.

Cumulative flux calculated using eq. (3) for 26 June 2007 between 8 and 18 UT is $-2.4 \mu$molCO2/m²s when only using aircraft observations ($s_{m-a}$) and $-3.0 \mu$molCO2/m²s when using both aircraft and tall tower observations ($s_{m-a+1}$). This cumulative flux has a streamwise length of 234 km and a lateral scale of 41 km, thus yielding an integration area of 9621 km², calculated using the Levy et al. (1999) expression shown in Section 2.1.

3.2.2. Entrainment flux. The entrainment flux at the top of the CBL is crucial when applying CBL budget methods (Culf et al., 1997; Schmitgen et al., 2004). Vertical velocity at the top of the ABL ($W_s$) is obtained by linear interpolation of vertical velocity profiles at the ABL height ($h$) extracted from NCEP-GFS analysis, and converted from pressure coordinates (Pas⁻¹) to z-coordinates (ms⁻¹) (Bakwin et al., 2004). Vertical velocity...
from reanalysis data have been successfully applied in regional CO₂ budget studies (e.g., Bakwin et al., 2004; Helliker et al., 2004; Lloyd et al., 2007; Wang et al., 2007). For 26–27 June, Wₖ is negative at LMU, that is, subsidence occurs in accordance with the synoptic situation. In anticyclonic episodes, conservation of air mass requires subsidence over highs to replace horizontally diverging air (Stull, 2000). However, it presents a clear diurnal variation, with minimum values at night (larger than −0.01 ms⁻¹ after 18 UT), and with those being maximum at 15 UT, with values of −0.04 ms⁻¹ (26 June) and −0.03 ms⁻¹ (27 June).

The entrainment flux for P1 and P2 is accounted by eq. (4). For P1, REFERENCETEXT is −1.2 μmolCO₂/m²s whereas it is 0.1 μmolCO₂/m²s for P2. Early in the morning the entrainment flux is larger, introducing air with low CO₂ concentrations from the FT down to the ABL, while in the mid-afternoon the entrainment brings air with higher CO₂ concentrations down to the ABL, resulting into a positive flux. The β-ratio calculated using the mean surface flux estimated by the CCI method by linear and exponential fits are 0.23–0.15 for P1 and (−0.02)–(−0.01) for P2. That is, during the morning, the entrainment process enters air masses with low CO₂ concentration from the FT down to the CBL associated with the rapid growth of the ABL. Conversely, during the afternoon, assimilation by the vegetation at the surface acts as a sink and there is an entrainment of air masses with higher concentrations from the FT that are mixed within the CBL air. Our results are therefore, in accordance with those reported in de Arellano et al. (2004). Thus, the ventilation processes driven by the entrainment phenomena appear to play an important role in the daytime evolution of CO₂ concentrations in the CBL. The mean entrainment flux taking place during the 10 h elapsed between the morning and the afternoon profiles is accounted by the second term in the eq. (3). This results into a mean entrainment flux of −0.8 μmolCO₂/m²s.

3.2.3. Results from the CCI method. Continuous CO₂ measurements from the morning and the afternoon profiles are averaged in 300-m layers between 900 and 2100 masl. The carbon flux crossing each of these layers (Iᵢ) is calculated applying eq. (6) and it is represented in Fig. 5. Iᵢ-values are fitted in altitude and extrapolated to the surface layer (Iₛ) for the Ebre region (~250 masl). As pointed in Section 2.2, the fitting equation used for extrapolation is related to the distribution in altitude of the carbon dioxide gradient. However, this gradient is seen not to follow a clear trend in altitude and therefore, linear and exponential approaches are considered. The linear fit of turbulent fluxes with height represents a good approximation (R² = 0.96; P < 0.05). However, as it can be observed in Fig. 5, the exponential fit gives an even slightly better approximation (R² = 0.9811; P < 0.05). Due to the low number of layers available, it is not possible, however, to distinguish whether the atmospheric dynamics follows either a linear or an exponential model. Both models are thus kept to extrapolate fluxes at the surface level and are given below as an additional measure of uncertainty in the estimates. Results of the mean regional surface flux yield values of −5.1 ± 0.1 and −7.9 ± 0.1 μmolCO₂/m²s from 8 to 18 UT on 26 June 2007, respectively, depending on whether the linear or the exponential function is used.

4. Discussion

The CO₂ content measured in the lowermost part of the vertical profiles is the result of diurnal changes in vegetation fluxes (photosynthesis/respiration) and of the CBL dynamics. Large concentrations close to the ground measured in the morning profile on 26 June 2007 arose both from the overnight respiration and the shallow boundary layer of the previous nocturnal boundary layer. As the sun warmed the ground, the ABL height increased, reaching its maximum around mid-afternoon. The CBL height then increased from ~970 to ~1326 magl (Table 1), leading to a change of the CO₂ content in the CBL. Simultaneously, vegetation with photosynthetic activity contributed further assimilating atmospheric CO₂. Furthermore, the entrainment of air with low CO₂ content from above the CBL further contributed to the decrease of atmospheric CO₂ mixing ratio. The profiles measured for the 27 June 2007 kept the nocturnal signal of low CBL height and respiration fluxes as CO₂ values are ~386 ppmv at 900 masl, but decreased faster in altitude than P1, reaching ~383.5 ppmv at ~2000 masl. The ABL height was ~1600 magl at the sampling time, and the dilution of the CO₂ concentration within the CBL was not complete. In the lowermost part of the profile, the CO₂ distribution kept the structure in an hourly time span, whereas CO₂ mixing ratios at higher levels experienced faster changes related to advection of upwind fluxes.

Results of the mean regional surface flux between the morning and the afternoon profiles calculated by the different approaches
from aircraft measurements are summarized in Table 2. Fluxes vary from $-7.9$ (CCI-exponential) to $-2.4$ $\mu$molCO$_2$/m$^2$s $^{-1}$ (ICBL $s_{m-a'; s_a}$). Large surface flux differences show up from the different methods used. In the following subsections, the uncertainty in the determination of cumulative fluxes from both methods used in this work is discussed (Sections 4.1 and 4.2).

The assumption of neglecting the advection in mass budget methods is pointed in Section 4.3. A general discussion about the flux values obtained in the Ebre watershed is presented in Section 4.4.

4.1. Uncertainty in the ICBL method

The uncertainty in the fluxes calculated using the ICBL method could be mainly attributed to the uncertainty of three parameters: the knowledge of the entrainment concentration; the average concentration in the boundary layer and the determination of meteorological parameters such as the boundary layer height or the vertical velocity at the top of it.

The insufficient accuracy in the determination of the entrainment concentration might contribute to an underestimation of the surface fluxes calculated by the ICBL technique. The value of the CO$_2$ concentration above the CBL is a critical measure when determining the surface flux from CBL CO$_2$ measurements (Culf et al., 1997; Schmitgen et al., 2004). CO$_2$ concentration in the air just above the CBL height in the morning flight on 26 June (s$_N$, Table 1) indicated the presence of a residual layer representing previous day’s nocturnal boundary layer. The measured concentration was 384.05 ± 0.24 ppmv, 1.7 ppmv larger than the FT concentration ($s_a$, Table 1) estimated from profiles on 27 June (382.36 ± 0.47 ppmv). Taking the CO$_2$ concentration of the residual layer ($s_N$) as the air entrained during CBL growth ($s_a$ in eq. (3)), the mean surface flux is $-4.3$ $\mu$molCO$_2$/m$^2$s $^{-1}$ (ICBL $s_{m-a'; S_a'; s_N}$), 1.8 times larger than ICBL $s_{m-a'; s_a}$ estimated using FT concentration ($s_a$, Table 1). This value is similar to the one calculated by the CCI-linear method which estimates a regional surface flux of $-5.1$ $\mu$molCO$_2$/m$^2$s $^{-1}$. The approach appears to be correct as the air entrained during the first hours of the day belongs to the mass just above the mixing layer. But residual layer entrainment usually occurs very quickly in the morning (Stull, 1988), so further CBL growth would require entrainment of free tropospheric air also (Styles et al., 2002) before convection is well established. As stated in Section 3.2.3, the entrainment flux is large during the early morning hours and decreases when the convective conditions are settled. Therefore, for the correct application of the ICBL method, there is a need to monitor the daily evolution of concentrations above the CBL to well determine the entrainment flux.

On the other side, calculation of $s_m$ assumes uniformity in the CBL column from the lowest aircraft altitude to the ground under convective situations. Nevertheless, the continuous in situ measurements could fill the gap between the lowest part of the profile and the surface. The surface flux using both aircraft plus tall tower observations (ICBL $s_{m-a'; s_a}$) by the ICBL method is $-3$ $\mu$molCO$_2$/m$^2$s $^{-1}$, therefore 1.25 times larger than that only considering aircraft measurements (ICBL $s_{m-a'; s_a}$; $s_a$; $-2.4$ $\mu$molCO$_2$/m$^2$s $^{-1}$).

Under convective situations, the parameter which influences more the ICBL calculations is the concentration used as $s_a$ rather than $s_m$. Therefore, the determination of the concentration above the CBL and its diurnal variation is critical to estimate regional surface fluxes from changes in measured mixing ratios within the boundary layer by the ICBL approach. The use of boundary conditions for the $s_a$ parameter from vertical profiles outside the domain or the MBL (Masarie and Tans, 1995) leads to underestimations of the regional surface fluxes. Hence, vertical profiles are needed that can sample the domain reaching enough altitude to ensure the proper coverage of the measurement of boundary conditions.

Higher resolution meteorological parameters or the use of direct observations of atmospheric structure obtained from ceilometers or FTIR instruments might equally improve the assessment of surface fluxes by the ICBL method. Particularly, the determination of the CBL height appears to be crucial in transport models used in inversion analysis (Tans et al., 1996; Gerbig et al., 2008). In this study, the CBL height is taken from the NCEP-GFS analysis as no radiosonde observations are available for those days. When comparing the 12UT CBL height calculated from radiosonde to the NCEP-GFS ones for June 2006, measures results into an overestimation of a 60% in the CBL height by the weather model. When correcting the CBL height by the radiosonde data, the mean surface flux is estimated by the ICBL method ($s_a$) to be $-2.3$ $\mu$molCO$_2$/m$^2$s $^{-1}$; thus, just $0.1$ $\mu$molCO$_2$/m$^2$s $^{-1}$ smaller. Then, the determination of the CBL height does not appear as a crucial factor in determining mean surface fluxes with this approach and in the region where applied.

Table 2. Calculated CO$_2$ surface flux (in $\mu$molCO$_2$/m$^2$s) according to the ICBL and CCI methods for 26 June 2007 between 8UT and 18 UT

| Method                  | Net surface flux | Entrainment flux |
|-------------------------|------------------|-----------------|
| ICBL $s_{m-a'; s_a}$   | $-2.4$           | $-0.8$          |
| ICBL $s_{m-a'; s_a}$   | $-3.0$           | $-0.8$          |
| ICBL $s_{m-a'; S_a}$   | $-4.3$           | $-0.4$          |
| ICBL $s_{m-a'; S_N}$   | $-4.8$           | $-0.5$          |
| CCI linear             | $-5.1$           |                |
| CCI exponential        | $-7.9$           |                |
| CarbonTracker-Europe   | $-8.4$           |                |

$s_{m-a'}$ CBL mixing ratio from aircraft observations; $s_{m-a'}$ CBL mixing ratio from both aircraft and tower observations; $s_a$ is extracted from the profile on 27 June 2007, at an altitude where no upwind surface fluxes influence is seen, as retrieved by the FLEXPART model; $s_N$ is the mixing ratio above the CBL height for P1.
Eventually, the mean surface flux is calculated by introducing \( s_N \) instead of \( s_{\text{sm}} \); once the aircraft, the tower observations in the CBL \((s_m-a_{\text{t}})\), and the correction of the CBL height by the radiosounding data is taken into account. The result is a cumulative flux of \(-4.1 \, \mu\text{mol CO}_2/\text{m}^2/\text{s}\). Including all the corrections and approaches above \((s_N, s_{\text{sm}}-a_{\text{t}} \text{ and CBL correction})\), it results into a 70% increase of the estimated surface flux.

### 4.2. Uncertainty in the CCI method

When using the CCI method, the fit of the turbulent fluxes in altitude determines the value of the surface flux, this introducing a large source of error when it is not set properly. In our study, both linear and exponential fits provide good approximations \((r^2 > 0.9; \, P < 0.05)\). However, the estimation of the flux at the surface level can result 55% apart depending on which fit function \( I_i \) used (Table 3). As a consequence, more sampling points taken within the 900–2100 m segment, and especially in the EZ, are needed to properly determine which equation best fits data.

Despite the former, CCI method seems a more robust approximation as without needing a proper characterization of the atmospheric structure, the surface flux estimates are closer to the ICBL method ones. In this case, ICBL values are obtained with a proper determination of the CBL concentration (here, aircraft profile plus tall tower measurements) and using \( s_N \) as the concentration of the entrainment air: \(-5.1 \, \mu\text{mol CO}_2/\text{m}^2/\text{s} \) (CCI-linear fit) and \(-7.9 \, \mu\text{mol CO}_2/\text{m}^2/\text{s} \) (CCI-exponential fit) are obtained, compared to \(-4.8 \, \mu\text{mol CO}_2/\text{m}^2/\text{s} \) (ICBL \( s_{\text{sm}}-a_{\text{t}} \); \( s_N \)).

### 4.3. Uncertainty due to advection

The influence of advection remains a source of uncertainty in the CBL budgeting approach as heterogeneous land cover and upwind anthropogenic emission sources can produce sufficiently large horizontal variability in the atmospheric CO2 mixing ratio to outweigh changes due to surface fluxes (Schmitgen et al., 2004). In some situations, it is therefore inappropriate to talk of a regional flux estimate derived from concentration changes observed at a point in space. CBL budget applied in a Canadian boreal forest showed that the horizontal transport cannot be neglected in the CBL mass budgeting for CO2 on a sub-synoptical scale (Shashkov et al., 2007). The degree of significance of the calculated fluxes depends on the heterogeneity of the atmospheric CO2 concentration field produced by the patchiness of biospheric sources and sinks and their response to the forcing meteorological drivers. As seen in Fig. 3, the CO2 distribution in the 100-km-stack around LMU is not completely homogenous during the morning and the afternoon transects, with variations in a range of 4.45 and 3.11 ppmv, respectively.

The advection term in a mass budget method is accounted as expressed in eq. (7):

\[
F_u = u \frac{\Delta C}{\Delta x}.
\]

where \( F_u \) is the flux due to the advection; \( u \) is the mean wind speed in the Ebre watershed during the survey; \( \Delta C \) is the standard deviation of the concentration measured in the 100 km horizontal transects and \( \Delta x \) is distance flown by the aircraft in the horizontal transects (100 km). Considering that the mean wind speed in the Ebre watershed was 5 ms\(^{-1}\) during the campaign, and taken into account the \( \Delta C \) for the morning and the afternoon transects (1.3 and 0.3 ppmv, respectively), it results into a flux due to advection of 0.15 \( \mu\text{mol CO}_2/\text{m}^2/\text{s} \) for the morning transect, and 0.05 \( \mu\text{mol CO}_2/\text{m}^2/\text{s} \) for the afternoon one. Thus, neglecting the flux due to advection represents an uncertainty ranging from 2 to 6% for the fluxes calculated by CBL mass budgets (Table 3).

The uncertainty due to advection depends mainly on the wind speed and the observed variability of CO2 concentration in the region where CBL techniques are applied (eq. 7). The Ebre basin is a very windy area where the wind speed can reach values of 28 ms\(^{-1}\) (\(-100 \, \text{km} \, \text{h}^{-1}\)). Considering different values of wind speeds for the same CO2 variability measured in the campaign in June 2007, and neglecting or not the advection term gives rise to a results spread within 36% of the uncertainty (for \( u \sim 30 \, \text{ms}^{-1}\)). Therefore, meteorological conditions should be carefully checked when CBL methods are applied, to avoid large errors in the flux calculations due to advection.

In addition, the homogeneity of the regional fluxes in the Ebre watershed can be checked by calculating cumulative fluxes from horizontal upwind transects. For that purpose, the mean CO2 concentrations are calculated for the horizontal transects at three longitudinal bands: 1–1.5 \( ^\circ \)W, 1.5–2 \( ^\circ \)W and 2–2.5 \( ^\circ \)W (Table 4). Meteorological parameters are obtained as explained in Section 3.2.1. The morning transect was sampled below the CBL whereas the afternoon one was obtained from within it. Then, the morning measurements are representative of the residual layer concentrations \( (s_N) \) rather than the CBL one. The mixing ratio in the CBL for the morning \( [s_N(t_1)] \) is taken from the hourly CO2 records at LMU tall tower. Measurements from the afternoon track are used to calculate the mean concentration in the CBL \( [s_N(t_2)] \). Applying eq. (3) and using the

### Table 3. Uncertainty arose by different terms when applying the ICBL and the CCI methods to estimate surface fluxes from changes in the CO2 concentration

| Term                          | ICBL        | CCI        |
|-------------------------------|-------------|------------|
| Entrainment concentration     | 99–57%      | –          |
| CBL concentration             | 26–12%      | –          |
| Boundary layer height         | 14–3%       | –          |
| Advection term                | 6–2%        | –          |
| Overall uncertainty           | 70%         | 55%        |

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CO2 values summarized in Table 4, the cumulative flux is −4.5 μmolCO2/m2s at 1–1.5°W; −4.9 μmolCO2/m2s at 1.5–2°W and −1.0 μmolCO2/m2s at 2–2.5°W (ICBLtrans). The values in the first two longitudinal bands considered are between those reported by ICBL (−4.3 μmolCO2/m2s) and ICBL’s −4.8 μmolCO2/m2s); and close to the calculated by the CCI-linear approach (−5.1 μmolCO2/m2s). The homogeneity of the surface fluxes in a 70 km transect, minimizes the uncertainty due to advection in the present study, making the conditions of the reported study suitable for the application of the CBL techniques. Therefore, for this synoptic situation, regional fluxes calculated from point anchored profiles (LMU) are representative of a 70-km-long transect (1° longitude at 41.60°N), as pointed by the similar surface fluxes estimated using vertical profiles over LMU and horizontal transects. The length scale of representative regional surface fluxes reported in this study is twice the length scale determined in the COBRA-2000 survey where ~30 km is stated to be the required resolution to fully resolve spatial variations of atmospheric CO2 in the boundary layer over the continent (Gerbig et al., 2003a). The scale covered by the measurements reported here is appropriate to investigate the homogeneity of the carbon fluxes over continental regions and provide additional insight to assess the appropriate resolution for global carbon fluxes inversion models.

4.4. Surface fluxes at the Ebre watershed

In this study, the first estimations of the regional surface fluxes in the Ebre watershed from aircraft and tall tower CO2 observations provide a first insight of the behaviour of this region in a global climate change context. The complexity of the land use in the region makes it appropriate the application of the CBL techniques as integrated regional surface fluxes are obtained. The surface flux estimated in the region responds to the fluxes of the mixed agricultural patches in the region (devoid of crops on the one hand and irrigated lands on the other) although the flux is dominated by the non-irrigated ones due to their prevalence in the central part of the Ebre watershed (see fPAR time series in Fig. 1c). June is a pretty active time for plant activity despite the fact that the most active months around LMU are April and May. Therefore, not very large uptaking fluxes were obtained in the region during the survey on late June 2007. Fluxes estimated from CBL techniques are compared with the surface flux from CarbonTracker-Europe (CTE; Peters et al., 2007, 2009) for the same source area of aircraft measurements during the time encompassing the morning and afternoon profiles (Fig. 6). CTE estimates a cumulative flux of −8.5 μmolCO2/m2s, therefore close to the value estimated by the CCI-exponential method in LMU (−7.9 μmolCO2/m2s).

The estimated surface values following different approaches indicate that the central part of the Ebre watershed was a weak sink of atmospheric CO2 during the central hours of June 2007. A modest sink of 0.2 GtC yr−1 equates to a net carbon flux of round −5 μmolCO2/m2s. More campaigns would, however, be needed to fully describe the annual CO2 flux of the Ebre ecosystem, encompassing diurnal and nocturnal fluxes as well as seasonal fluxes. However, this study provides the first insight and approximates the order of magnitude of the surface fluxes in the region. Even considering the regional surface flux in a pretty active period of the year as it is in June (Fig. 1c), the Ebre watershed would be located in the lower range of European sink fluxes according to Denman et al. (2007), which points to a flux of (−0.9 to +0.2 GtC yr−1) for the European ecosystems estimated by inversion models.

5. Conclusions

Carbon regional surface fluxes in the central part of the Ebre watershed have been estimated using the ICBL and CCI methods at La Muela site (LMU) on 26 June 2007 between 8 and 18 UT. The surface flux values range from −2.4 to −7.9 μmolCO2/m2s. The surface flux is representative of the western region of the Ebre watershed with a total surface area of ~2 × 105 km2, that is, a length scale of ~102 km. For the period encompassed, the central part of the Ebre watershed behaves as a net sink of atmospheric CO2.

Variability in estimated fluxes depends on the CO2 observations considered to calculate the mean concentration in the CBL and those above it. The ICBL estimates yield a net surface flux of −2.4 and −3.0 μmolCO2/m2s considering either only aircraft observations or both aircraft and tower observations, respectively, and taking the FT concentration measured on vertical profiling on 27 June 2007. When the residual air is considered to be entrained into the CBL (sN), it results into a mean surface flux of −4.3 and −4.8 μmolCO2/m2s, respectively. Thus, the entrainment processes appear to be a key parameter at the
very early hours of the morning, and then it is important to track changes in concentrations just above the CBL to precisely calculate surface fluxes using the ICBL formulation—when convective conditions prevail. The CCI method instead, estimates a mean surface flux of \(-5.1\) and \(-7.9\) \(\mu\text{molCO}_2/\text{m}^2\text{s}\), when considering a linear or exponential fit of the turbulent fluxes in altitudes for extrapolation, respectively. The uncertainty linked to the ICBL method is 70\% whereas it is 55\% for the CCI, making the latter a more robust technique. Surface fluxes calculated from ICBL and CCI approaches are then compared with the fluxes given by the assimilation system of CTE. For the time encompassed between profiles, CTE estimates a mean surface flux of \(-8.5\) \(\mu\text{molCO}_2/\text{m}^2\text{s}\), close to the CCI-exponential approach \((-7.9\ \mu\text{molCO}_2/\text{m}^2\text{s})\). However, the CCI-linear approach calculates similar values to the ICBL technique taking the residual concentration entrained into the CBL (ICBL\(_{\text{res}}\)) and measurements from horizontal transects (ICBL\(_{\text{trans}}\)) in one longitudinal degree area. However, the fact that results from CET and CCI-exponential are similar enhances our confidence that the assimilation system of CTE works properly to calculate fluxes in NE Spain.

In sum, the Ebre watershed can be considered to act as a weak sink of CO\(_2\), with a total amount uptake of 0.2GtC yr\(^{-1}\), if considering only the surface fluxes calculated in this study. More studies are, however, needed to precisely assess the role of the Ebre watershed in the uptake of atmospheric CO\(_2\) mixing ratios. However, the values presented in this study are the first ones ever obtained for the Mediterranean region and provide a first insight on the likely role these semiarid regions can play in the regional modulation of global carbon fluxes.

6. Acknowledgments

The authors are especially grateful to Álvaro Lapetra for the smooth aircraft navigation during the flight campaign in NE Spain on June 2007. The authors also want to thank the Wageningen University that in collaboration with the CarboEurope partners provided the CarbonTracker-Europe results of the surface fluxes (http://www.carbontracker.eu). The ICARO-II aircraft program was funded by the Spanish Ministry of Science and Education, project no. CGL12398.
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