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TELLUS

Regional carbon dioxide fluxes from mixing ratio data

By P. S. BAKWIN[1]*, K. J. DAVIS[2], C. YI[2], S. C. WOFSY[3], J. W. MUNGER[3], L. HASZPRA[4] and Z. BARCZA[5], [1]*Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA;* [2]*Department of Meteorology, The Pennsylvania State University, University Park, PA, USA;* [3]*Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA;* [4]*Department for the Analysis of Atmospheric Environment, Hungarian Meteorological Service, Budapest, Hungary;* [5]*Department of Meteorology, Eötvös Loránd University, Budapest, Hungary*

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ABSTRACT

We examine the atmospheric budget of CO_2 at temperate continental sites in the Northern Hemisphere. On a monthly time scale both surface exchange and atmospheric transport are important in determining the rate of change of CO_2 mixing ratio at these sites. Vertical differences between the atmospheric boundary layer and free troposphere over the continent are generally greater than large-scale zonal gradients such as the difference between the free troposphere over the continent and the marine boundary layer. Therefore, as a first approximation we parametrize atmospheric transport as a vertical exchange term related to the vertical gradient of CO_2 and the mean vertical velocity from the NCEP Reanalysis model. Horizontal advection is assumed to be negligible in our simple analysis. We then calculate the net surface exchange of CO_2 from CO_2 mixing ratio measurements at four tower sites. The results provide estimates of the surface exchange that are representative of a regional scale (i.e. $\sim 10^6$ km^2). Comparison with direct, local-scale (eddy covariance) measurements of net exchange with the ecosystems around the towers are reasonable after accounting for anthropogenic CO_2 emissions within the larger area represented by the mixing ratio data. A network of tower sites and frequent aircraft vertical profiles, separated by several hundred kilometres, where CO_2 is accurately measured would provide data to estimate horizontal and vertical advection and hence provide a means to derive net CO_2 fluxes on a regional scale. At present CO_2 mixing ratios are measured with sufficient accuracy relative to global reference gas standards at only a few continental sites. The results also confirm that flux measurements from carefully sited towers capture seasonal variations representative of large regions, and that the midday CO_2 mixing ratios sampled in the atmospheric surface layer similarly capture regional and seasonal variability in the continental CO_2 budget.

1. Introduction

Several independent lines of evidence indicate that there is a large and highly variable sink for atmospheric CO_2 to terrestrial ecosystems at temperate latitudes of the Northern Hemisphere. The evidence includes analysis of the spatial pattern of CO_2 mixing ratios (Tans et al., 1990; Conway et al., 1994), interpretation of the global data set of $^{13}C/^{12}C$ ($\delta^{13}C$) in atmospheric CO_2 (Ciais et al., 1995), measurements of the atmospheric O_2/N_2 ratio (Keeling et al., 1996; Battle et al., 2000), direct observation of net uptake of CO_2 by many forest ecosystems throughout Europe (Valentini et al., 2000) and North America (Baldocchi et al., 2001), and inventory estimates of carbon accumulation in terrestrial ecosystems (Houghton, 1999; Pacala et al., 2001). Accumulation of carbon by northern terrestrial ecosystems is consistent with an observed increase in the duration of the summertime draw-down of atmospheric CO_2 at northern latitudes (Randerson et al., 1999), and with satellite observations showing increased length of the growing season and overall greening of northern lands (Myneni et al., 1997). Nevertheless, we still do not have a clear understanding of which terrestrial systems are accumulating carbon and the processes contributing substantially to carbon uptake. This information is urgently needed to develop strategies to effectively manage carbon sequestration by the terrestrial biosphere in order to slow the accumulation of CO_2 in the atmosphere (Wofsy and Harriss, 2002).

Direct measurements of the atmosphere/biosphere exchange of CO_2 (net ecosystem exchange, NEE) are being made at dozens of sites worldwide with the goal of understanding how terrestrial ecosystems respond to environmental changes such as climate change, land use, pollution and increased atmospheric CO_2. These studies, which are coordinated under the FLUXNET programme (Baldocchi et al., 2001), address NEE on rather

*Corresponding author.
e-mail: peter.bakwin@noaa.gov

small spatial scales, typically a few hectares, and it is difficult to extrapolate the results to large regions such as countries or continents.

Estimates of annual CO_2 exchange on a continental scale have been made using inverse model techniques (Fan et al., 1998; Rayner et al., 1999; Bousquet et al., 2000; Gurney et al., 2002). These models all rely on measurements of CO_2 mixing ratios made primarily in remote marine locations and on the tops of mountains, which are rather insensitive to exchange taking place on the continents. The result is that inverse models that partition the terrestrial sink between the northern continental areas have had very large uncertainty bounds.

Measurements of CO_2 are clearly needed over the continents to improve estimates of regional net exchange of CO_2 with the terrestrial biosphere (Tans et al., 1996; Rayner et al., 1996; Running et al., 1999; Gloor et al., 2000). Gloor et al. (2001) assessed the spatial scale that is represented by measurements of the trace gas mixing ratio at a continental tower site by using measurements of the industrial solvent C_2Cl_4, demographic data as a proxy for the spatial distribution of C_2Cl_4 sources, and a trajectory model. They found that the tower measurements are sensitive to emissions over an area of roughly 10^6 km^2. However, sources of C_2Cl_4 were mainly distant from the tower. Because of large proximate sources and sinks of CO_2 in terrestrial systems, CO_2 mixing ratios are extremely variable on short time scales near the ground. For example, a huge (tens of parts per million, ppm) diurnal cycle typically exists during the growing season resulting from the covariation of biotic activity (net uptake of CO_2 during daytime, net loss of CO_2 from the biosphere at night) and atmospheric vertical mixing (deep during daytime, shallow at night) (Leith, 1963; Bakwin et al., 1998a). Helliker et al. (2003) showed that monthly averaging of CO_2 concentration measured in the well-mixed region of the atmospheric boundary layer (ABL) from a 400 m tower revealed consistent standing differences of several ppm between the CO_2 concentration of the ABL and that of the free troposphere above. They showed that very reasonable estimates of monthly-integrated surface CO_2 flux over the region sampled by the WLEF television transmitter tower (see Section 2) could be obtained by analysis of these average gradients and estimates of the rate of vertical mixing of between the ABL and free troposphere.

We examine CO_2 mixing ratio and atmosphere/surface exchange data from four temperate continental sites. For each site we construct a simple CO_2 budget for the lower atmosphere that includes surface exchange, a rate of change term and horizontal and vertical advection. We approximate advection as vertical exchange between the ABL and free troposphere and estimate it at each tower site by using a residence time for air in the ABL that is derived from modelled mean vertical velocities from the NCEP Reanalysis. This allows us to estimate the CO_2 surface flux on a regional scale directly from CO_2 mixing ratio data. The resulting fluxes are in reasonable accord with local-scale fluxes measured at the towers by using eddy covariance methods, and with accounting for contribution of combustion emissions within the larger area represented by the mixing ratio data. The results give us confidence that measurements of CO_2 mixing ratios on continental towers represent a useful database for inverse model studies at the regional scale as envisioned by the North American Carbon Plan (Wofsy and Harriss, 2002) and by the CarboEurope project (http://www.bgc-jena.mpg.de/public/carboeur/), and suggest a method for estimating regional scale surface exchange directly from a network of tower sites and aircraft observations. At present CO_2 mixing ratios are measured with sufficient accuracy relative to World Meteorological Organization (WMO) standards at only a few continental sites.

2. Sites

Accurate CO_2 mixing ratio data were available from four tower sites where NEE was also measured. The sites are the 447 m tall WLEF television transmitter tower in Northern Wisconsin, USA (45.95°N, 90.27°W, hereinafter referred to as LEF), the Harvard Forest Environmental Measurement Site in Central Massachusetts, USA (42.52°N, 72.18°W, HVD), the Old Black Spruce site of the BOREAS Northern Study Area near Thompson, Manitoba, Canada (55.88°N, 98.48°W, OBS), and the Hegyhátsál, Hungary, tower site (46.95°N, 16.65°E, HUN). All of the sites are within the temperate to boreal zone of the Northern Hemisphere, where climate is highly seasonal and prevailing winds are generally westerly, with stronger zonal winds typical in winter than in summer.

The LEF site is in a region of cold temperate mixed forest with abundant wetlands. The vegetation assemblage has been described previously (Bakwin et al., 1998a; Mackay et al., 2002). Measurements of CO_2 mixing ratios have been on-going since October 1994 (Bakwin et al., 1998a). The forest surrounding the tower is similar to the typical landscape for at least 200 km to the west and east, and about 100 km to the north and south. At greater distances to the south agriculture is common, and Lake Superior lies 70–100 km to the north. Measurements of NEE showed that the mixed forest landscape was in approximate carbon balance with the atmosphere during 1997 (Davis et al., 2003). The tower is a key site in the Chequamegon Ecosystem Atmosphere Study which focuses on understanding the factors controlling the net exchange of CO_2 of the regional forest ecosystems (see the September 2003 special issue of *Global Change Biology*). In summer the LEF site often lies at the northern extent of a monsoonal flow into the continent from the Gulf of Mexico, and therefore in summer air flow from the south is somewhat more common than in other seasons.

The HVD site is located in a temperate hardwood forest dominated by oak and maple. The region surrounding the tower is heterogeneous, consisting of forests, farms and cities of various sizes. The forest itself is reasonably similar to many forests of the Northeastern USA. A very high degree of correlation existed

during 1995–2000 between measurements of NEE at HVD and at Howland Forest, an evergreen forest site about 400 km to the northeast, indicating that changes in NEE at these two physiologically different forests are driven by the same climate anomalies (D. Hollinger, personal communication, 2002). Measurements of CO_2 mixing ratios and NEE have been made at HVD since 1990 (Wofsy et al., 1993; Goulden et al., 1996a,b), and the forest accumulated 2.0 ± 0.4 tC ha^{-1} yr^{-1} during 1993–2000 (Barford et al., 2001). The influence of air mass trajectory on trace gas composition measured at HVD has been analysed in detail by Moody et al. (1998).

The HUN site is located in Western Hungary in a rural region of mixed agriculture and forest, which is very similar to much of the Carpathian Basin (>300 000 km^2). The site and measurements are described by Haszpra et al. (2001). Measurements of CO_2 mixing ratios and NEE began in September 1994 and April 1997, respectively. During 1997–1999 the landscape accumulated an average of 1.0 tC ha^{-1} yr^{-1} (Z. Barcza and L. Haszpra, unpublished data). Haszpra (1999b) showed that CO_2 mixing ratios measured in the afternoon at HUN correlate very well with those measured at the Hungarian K-puszta site about 220 km to the east. More information on the HUN site and surrounding region, and CO_2 measurements at HUN and K-puszta is given in Haszpra (1999a,b) and Haszpra et al. (2001).

The OBS site is an open-canopy boreal black spruce forest with an understorey dominated by feather and sphagnum mosses. The landscape for many hundreds of kilometres in every direction is a patchwork of forest stands of varying ages, with fire as the main disturbance. The stand in the immediate vicinity of the OBS tower is relatively old, having last burned about 120 yr ago. The OBS site is much less productive than the other three, and was in approximate carbon balance with the atmosphere during 1994–1997, losing 0.3 ± 0.5 tC ha^{-1} yr^{-1} (Goulden et al., 1998).

3. Budget calculations

Our analysis focuses on processes that influence the budget of CO_2 in the continental atmosphere on monthly and seasonal time scales. Large and rapid changes in the CO_2 mixing ratio at the towers are associated with the passage of synoptic weather systems which bring air of different histories to the sites. The influence on CO_2 of several synoptic events at LEF has been examined in detail in Hurwitz et al. (2004). Biogenic surface fluxes (NEE) are also affected by synoptic events. Here we are interested in the budget of CO_2 on longer time and larger spatial scales so we form monthly means to average out variations on the synoptic time scale while preserving the seasonal cycles of NEE and mixing ratio. Selecting other averaging intervals long enough to smooth over the synoptic variations does not change our results appreciably.

The budget equation for CO_2 in the ABL, Reynolds averaged over the time scale of turbulent eddies, can be written

$$\frac{\partial C}{\partial t} + \frac{RT}{p}\frac{\partial F_C}{\partial z} + W\frac{\partial C}{\partial z} + U\frac{\partial C}{\partial x} = 0 \tag{1}$$

where C is the molar CO_2 mixing ratio (in units of μmol CO_2 per mol dry air, ppm), R is the universal gas constant (Pa m^3 K^{-1} mol^{-1}), T is temperature (in K), p is pressure in Pa), F_C is the net turbulent flux of CO_2 (μmol m^{-2} s^{-1}), which includes both biogenic (NEE) and anthropogenic (fossil fuel) fluxes, U and W are the mean horizontal and vertical wind speeds and x and z are the horizontal and vertical coordinates. We have assumed no source of CO_2 in the atmosphere. For simplicity of presentation in the following we incorporate RT/p into the fluxes (F_C), giving units of ppm m s^{-1}. We integrate (1) over a vertical layer whose depth is the maximum daytime depth of the ABL, z_i, apply the continuity equation and the condition that $W = 0$ at the Earth's surface, and divide by z_i, to find

$$\left\langle \frac{\partial C}{\partial t} \right\rangle - \frac{F_C^0}{z_i} + \frac{F_C^{z_i} + WC|_{z_i}}{z_i} + \left\langle U\frac{\partial C}{\partial x} \right\rangle = 0 \tag{2}$$

where angled brackets represent averages over the layer of thickness z_i, F_C^0 is the surface flux and F_C^{zi} is the turbulent flux across the top of the layer, referred to as entrainment in the micrometeorological literature. We now average this equation over a period of 1 month, assume that horizontal advection can be neglected on this time scale, and approximate the monthly mean vertical exchange between ABL air and the free troposphere (FT), the third term in eq. (2), as

$$\frac{\overline{F_C^{z_i}} + \overline{WC|_{z_i}}}{z_i} = \frac{\overline{\langle C\rangle} - \overline{C_{FT}}}{\tau} \tag{3}$$

where τ is the residence time of air in the ABL and the overbar represents an average over 1 month. By eq. (3), we represent the free troposphere as a large reservoir of CO_2 that changes slowly (relative to the ABL) in response to surface exchange. Over this time scale the ABL depth should be thought of as the mean daytime maximum depth (Chou et al., 2002) and the terms representing vertical exchange between the ABL and FT include the effects of synoptic storms and deep, moist convection. The budget equation, eq. (2), becomes

$$\overline{\left\langle \frac{\partial C}{\partial t} \right\rangle} - \frac{\overline{F_C^0}}{z_i} = \frac{\overline{C_{FT}} - \overline{\langle C\rangle}}{\tau} \tag{4}$$

where we have moved the vertical exchange term to the right-hand side of the equation. The residence time, τ, can be expressed as $\tau = zi/w_M$, where w_M is the monthly mean (unsigned) magnitude of the vertical velocity at z_i. If we assume that the covariance between F_C^0 and z_i is negligible (demonstrated below), we can solve for the monthly averaged surface flux,

$$\overline{F_C^0} = (\overline{\langle C\rangle} - \overline{C_{FT}})w_M + \overline{\frac{\partial\langle C\rangle}{\partial t}}\,\overline{z_i}. \tag{5}$$

Note that we have also interchanged the averaging over the ABL depth and time derivative in the CO_2 storage term. In the following we dispense with the overbars and brackets; monthly averaging and vertical integration over the ABL are implied.

Changes in trace gas mixing ratios at a site are influenced by processes occurring for a few hundred kilometres upwind (Gloor et al., 2001). Hence, eq. (5) provides a framework to estimate net surface fluxes (F_C^0) over a large region. We evaluate the use of eq. (5) to calculate F_C^0 using data from the four flux tower sites and the global CO_2 monitoring network.

4. Measurements and data

Mixing ratios of CO_2 were measured using non-dispersive infrared gas analysers (IRGAs) from LiCor, Inc. All IRGAs were calibrated frequently against compressed gas standards that are directly traceable to standards maintained by the WMO Central Calibration Laboratory for CO_2, which is located at NOAA/CMDL in Boulder, CO, USA (Zhao et al., 1997). The data are reported as mole fractions relative to dry air (ppm). NEE was measured at all sites using eddy covariance methods as described in the references cited above.

During the growing season a large diurnal cycle of the CO_2 mixing ratio is observed in the atmospheric surface layer, the lowest several tens of metres above the ground. At night CO_2 from respiration is trapped in a shallow, stable layer of air near the ground and CO_2 mixing ratios in excess of 400 ppm and high variance are often observed. This build-up is typically not observed above 200–300 m, as higher altitudes are decoupled from the surface at night by a low-level inversion (Bakwin et al., 1995, 1998a). During the daytime convection nearly homogenizes the mixed layer, which is typically 1–2 km deep (Yi et al., 2001). In the afternoon vertical gradients of CO_2 in the lowest 400–500 m are typically 1–2 ppm (Bakwin et al., 1998a). For this analysis we use daily (24 h) mean CO_2 measurements from 396 m above the ground on the LEF tower as representative of the lowest 1–2 km of the atmosphere. For HVD, HUN and OBS, where measurements were made on relatively short towers (30 m at HVD and OBS, 115 m at HUN), we use CO_2 mixing ratio data from afternoon periods when vertical gradients are at a minimum. With strong vertical mixing the afternoon values are most likely to be representative of a large area rather than being mainly influenced by local surface exchange (Haszpra, 1999b; Potosnak et al., 1999). For the short towers we adjusted the CO_2 mixing ratios to mid-ABL values by using flux-gradient relationships for the convectively mixed ABL (Davis et al., 2000). These adjustments, which ranged from about −0.3 (HVD and HUN in winter) to + 2.5 ppm (HVD in summer), are small relative to the large-scale horizontal and vertical gradients (Fig. 1), and had a minimal effect on the results.

Monthly means of $\partial C/\partial t$ were computed from smooth curve fits (Fig. 2) to the daily values using the method of Thoning et al. (1989) (Table 1). More details on the statistics of the curve fits at LEF are presented by Bakwin et al. (1998a).

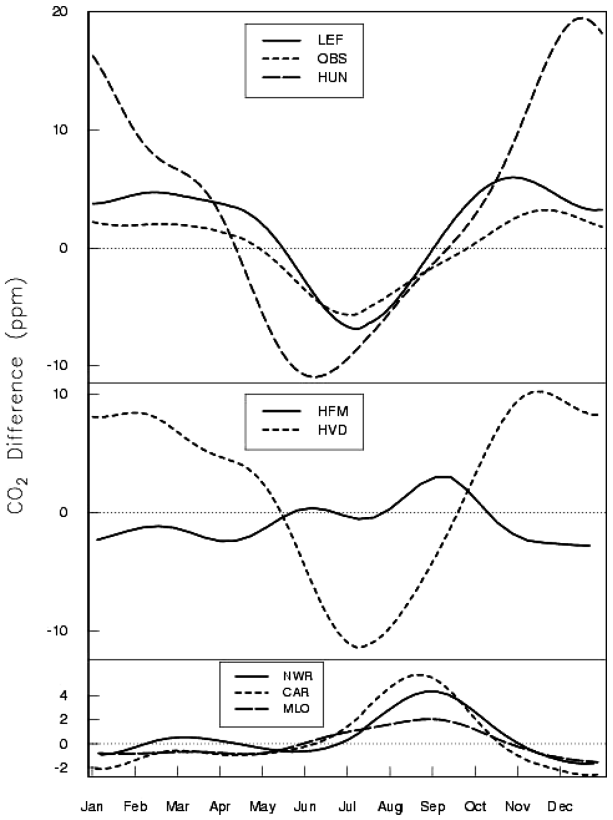

Fig 1. Difference between CO_2 mixing ratio at various locations and the MBL at the same latitude (from GLOBALVIEW, 1999). Sites are the four towers discussed in this paper, plus: NWR, a mountain site at 3.5 km altitude at Niwot Ridge, CO; CAR, aircraft data from 5 km over north-central Colorado; HFM, aircraft data from 4.5 km over HVD; MLO, the Mauna Loa Observatory in Hawaii (3.4 km altitude). MLO is included to show a measure of the vertical gradient over the ocean. Sites are separated into different panels for clarity of presentation, but the scales are identical. HFM and HVD are shown together (middle panel) because they represent different atmospheric layers (FT and ABL, respectively) at the same location, otherwise ABL sites are shown in the top panel and FT sites are in the lower panel.

To calculate $C - C_{FT}$ we need measurements of CO_2 within and above the ABL at the tower sites. The tower data give a direct measure of the CO_2 mixing ratio in the ABL, C (after a small correction at the short towers, as above). Mixing ratios of CO_2 in the FT have been monitored regularly at only a few locations in North America, including the mountain site (3.5 km elevation) at Niwot Ridge, CO (NWR, since 1967), and aircraft flights over north-central Colorado (CAR, every 1–2 weeks since 1992) and over the HVD site (HFM, about every 3 weeks since late 2000) (NOAA/CMDL, unpublished data). No long-term aircraft data were available from over Europe. Regular aircraft flights over LEF and HUN have begun recently, but these

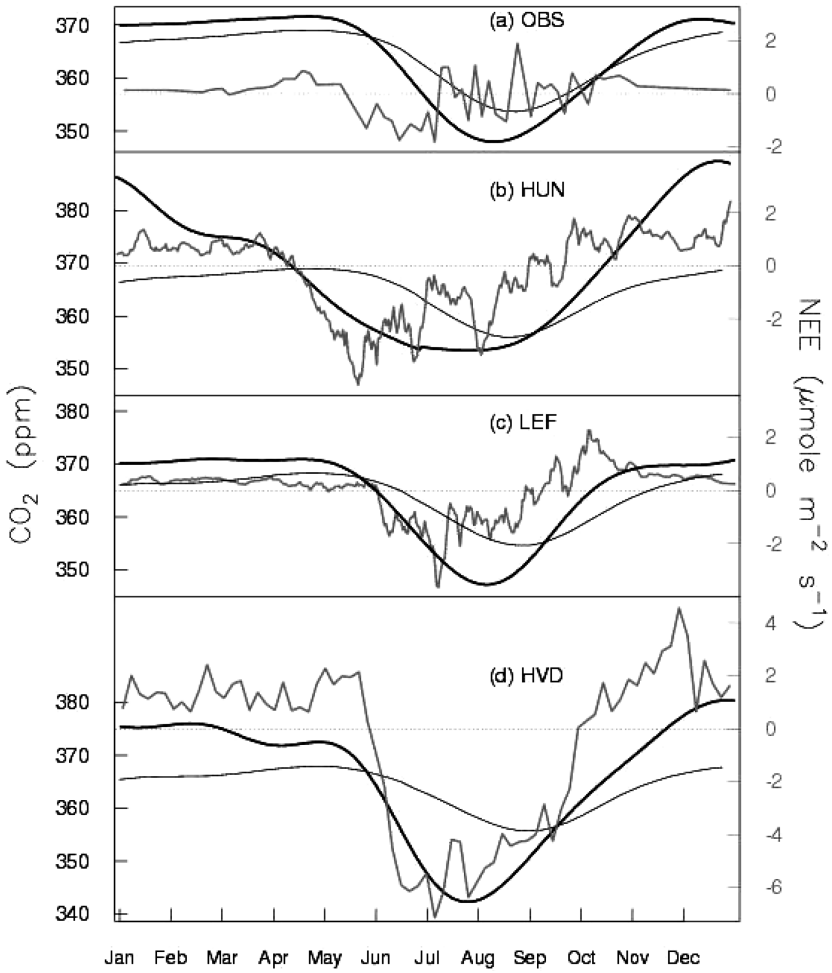

Fig 2. Mixing ratios and NEE of CO_2 at (a) OBS, (b) HUN, (c) LEF and (d) HVD. Data for OBS, HVD and LEF are for 1997, while HUN data are a composite from 1998 and 1999. CO_2 mixing ratios at HUN have been adjusted to account for the Northern Hemisphere mean rate of increase of CO_2 in order to be comparable to the other sites. Daily measurements of CO_2 mixing ratios have been fitted with a smooth curve (thick black line) after the method of Thoning et al. (1989). Grey lines are local NEE data (tower eddy fluxes) that have been smoothed with a running mean filter with a 5-day time constant for the purposes of illustration. Positive NEE values indicate that the vegetation is a source of CO_2 to the atmosphere. The thin lines represent CO_2 mixing ratios in the MBL at the latitudes of the tower sites (GLOBALVIEW, 1999). Scales for each tower are identical.

Table 1. Monthly values of terms in eq. (3) at LEF (1997), and local NEE from the tower eddy fluxes. Units are μmol m^{-2} s^{-1}

Month	$w_M(C - C_{FT})$	$z_i \partial C/\partial t$	F_C^0	NEE
Jan	1.1	0.0	1.1	0.4
Feb	0.8	0.0	0.9	0.4
Mar	1.2	0.0	1.2	0.4
Apr	0.6	0.0	0.6	0.3
May	0.2	−0.2	0.1	0.2
Jun	−1.0	−0.3	−1.2	−1.2
Jul	−1.9	−0.2	−2.1	−1.7
Aug	−1.2	0.1	−1.1	−1.0
Sep	0.3	0.2	0.5	0.4
Oct	1.1	0.1	1.2	1.3
Nov	0.9	0.0	0.9	0.6
Dec	0.4	0.0	0.4	0.4

data sets are still too short for our present purposes. Gradients of CO_2 between the MBL and the continental FT are generally somewhat smaller than those between the MBL and the continental ABL (Fig. 1). Hence, lacking direct measurements of C_{FT} over the towers during 1997 (LEF, HVD, OBS) and 1998–1999 (HUN), we use as proxies data from the MBL at the latitude of each tower and alternatively from 5 km altitude at CAR. Comparison of results using these two data sets to estimate C_{FT} over the towers gives an idea of the uncertainty introduced into the calculation of F_C^0. The MBL reference includes data from sites in both the Atlantic and Pacific Ocean basins, but monthly mean Atlantic and Pacific data at the same latitude typically differ by less than 1 ppm (P. Tans, NOAA/CMDL, personal communication, 2002).

Helliker et al. (2003) also recognized the importance of vertical advection in the budget of CO_2 in the ABL. They used data from our Wisconsin tower site (LEF), and estimated vertical advection by analysis of the budget of water vapour in the ABL with the surface flux of water vapour measured by eddy covariance. As in our analysis, Helliker et al. (2003) used the MBL data to estimate C_{FT}. Helliker et al. (2003) compared vertical exchange derived using water vapour observations with those derived from reanalysis, and showed that these are similar in fair weather conditions but that the Reanalysis-derived exchange velocity is substantially smaller than that derived using a water vapour budget.

Their work was the first to show that very reasonable estimates of the surface flux of CO_2 could be obtained by this method for the region around LEF, indicating that a quantitative estimate of the vertical exchange term can be obtained from simple data and that vertical exchange is probably dominant over horizontal. Our analysis differs from that of Helliker et al. (2003) in several important ways: (1) our estimates of w are taken from the Reanalysis data; (2) we include the $\partial C/\partial t$ term; (3) we analyse data from three additional tower sites; and (4) Helliker et al. (2003) did not consider the influence of anthropogenic CO_2 emissions on F_C, as compared to NEE.

For each tower site we estimate w_M as the monthly mean of the absolute value of daily vertical velocity from the NCEP Reanalysis product (Kalnay et al., 1996), which we have interpolated to the height of the ABL top (z_i) and converted from pressure coordinates (Pa s^{-1}). Resolved vertical velocity in the NCEP model balances horizontal divergence, and represents a grid-cell (about 200×200 km) average value. The model parametrizes the major physical processes involving vertical motions, including deep and shallow convection, large-scale precipitation, gravity wave drag, radiation and radiative effects of clouds, boundary layer dynamics, surface hydrology and vertical and horizontal diffusion. Subgrid convective mixing is simulated but is not included in the grid-cell mean vertical velocity.

Yi et al. (2001) estimated z_i at LEF using measurements from an ABL radar system. The measurements were made during March–November 1998 and z_i was estimated for the winter months by using an empirical fit to the surface buoyancy flux. Monthly mean values of z_i varied from 1.0 km in winter (November–February) to 2.0 km in May. Haszpra (1999a) estimated the monthly mean (1987–1992) of z_i for a suburban site near Budapest, Hungary. Mean afternoon z_i ranged from 0.6 km in winter to 1.5 km in summer. Mixed layer depths at HUN are expected to be very similar. Radiosondes were used to measure z_i at OBS frequently during three intensive field campaigns as part of the BOREAS Project in May–September 1994 (Barr and Betts, 1997). The BOREAS data show z_i values and seasonal changes that are very similar to the LEF observations. We lack direct observations of z_i at HVD. For the present work we use the monthly mean of measurements of z_i from LEF in 1998 (Yi et al., 2001) for LEF, HVD and OBS, and for HUN we use the Budapest data (Haszpra, 1999a). Values of $z_i\ \partial C/\partial t$ are generally small compared with $w_M(C - C_{FT})$ (Table 1). Values of w_M from NCEP also depend on altitude, typically decreasing by 15–30% from the 700 mbar to 850 mbar, while z_i is usually in the range of 760–860 mbar at our sites. Hence, our estimates of F_C^0 depend on z_i only weakly.

Since ABL convection is forced by the surface buoyancy flux, z_i exhibits a seasonal cycle with a maximum in spring and minimum in winter (Stull, 1988; Yi et al., 2001). Of course, z_i also varies with the weather conditions. Using a trajectory model Moody et al. (1998) estimated that z_i averaged for different synoptic classifications at HVD varied by a factor of two (875 to 1780 m), but for classes representing 63% of all occurrences average z_i was very consistent in the range of 1200–1250 m.

It is likely that F_C^0 and z_i are correlated on synoptic time scales, which would require an additional term in eq. (5). For example, in summer the passage of a synoptic disturbance can temporarily increase the mixing depth, often to near the depth of the troposphere, while net uptake by the vegetation is suppressed due to cloudy conditions. During disturbed weather the radar system is often unable to unambiguously determine z_i, which may be poorly defined. Without a means to estimate z_i for all time periods we cannot evaluate the magnitude of this covariance. As a rough estimate let us assume that in summer z_i equals 2 km and 10 km during fair and disturbed weather, respectively, and F_C^0 equals -3 and -1 μmol m^{-2} s^{-1} as a 24 h mean during these conditions. If fair and disturbed conditions occur with equal frequency then there is a covariance term of $+0.5$ μmol m^{-2} s^{-1}, roughly half the magnitude of the value of $w_M(C - C_{FT})$ in summer (Table 1). The true covariance will almost certainly be much smaller than this since disturbed conditions occur for less than half the time and since F_C^0 and z_i are not perfectly correlated. In winter the biogenic component of F_C^0 (mainly soil respiration) responds weakly to synoptic conditions since soil temperatures change relatively slowly. Hence, using monthly mean values of F_C^0 and z_i is a reasonable first approximation.

5. Results

At LEF, HVD and HUN ABL CO_2 mixing ratios and local surface fluxes are out of phase: CO_2 mixing ratios start to decrease rapidly in spring about 20–30 days before the vegetation begins taking up CO_2 in net, and similarly CO_2 increases in the autumn 1–2 months before the forest becomes a net source for CO_2 to the atmosphere (Fig. 2). These patterns indicate that advection plays a role in the budget of ABL CO_2 at these sites, at least during spring and autumn. At OBS NEE is more closely in phase with CO_2 mixing ratios, and NEE values are much smaller than at the other sites.

Equation (5) allows us to use CO_2 mixing ratio measurements from tower sites to estimate the regional surface flux of CO_2, F_C^0, which includes both biotic exchange and anthropogenic emissions. The results represent an estimate of the net surface exchange on a regional spatial scale, i.e. $\sim 10^6$ km^2. At LEF and HUN F_C^0 is in reasonable accord with the local scale flux measured by eddy covariance (NEE) during the spring, summer and autumn seasons (Figs 3b and c). Though the spatial scales represented by these two flux estimates are very different there is reason to expect that eddy flux data from the LEF and HUN towers should be fairly representative of the larger regions. These results give some confidence that the regional flux estimates are reasonable. At OBS in summer the regional flux (F_C^0) indicates much more uptake by the vegetation than the local NEE (Fig. 3a), while at HVD F_C^0 indicates somewhat less summertime uptake than the local NEE (Fig. 3d). These results are in agreement with

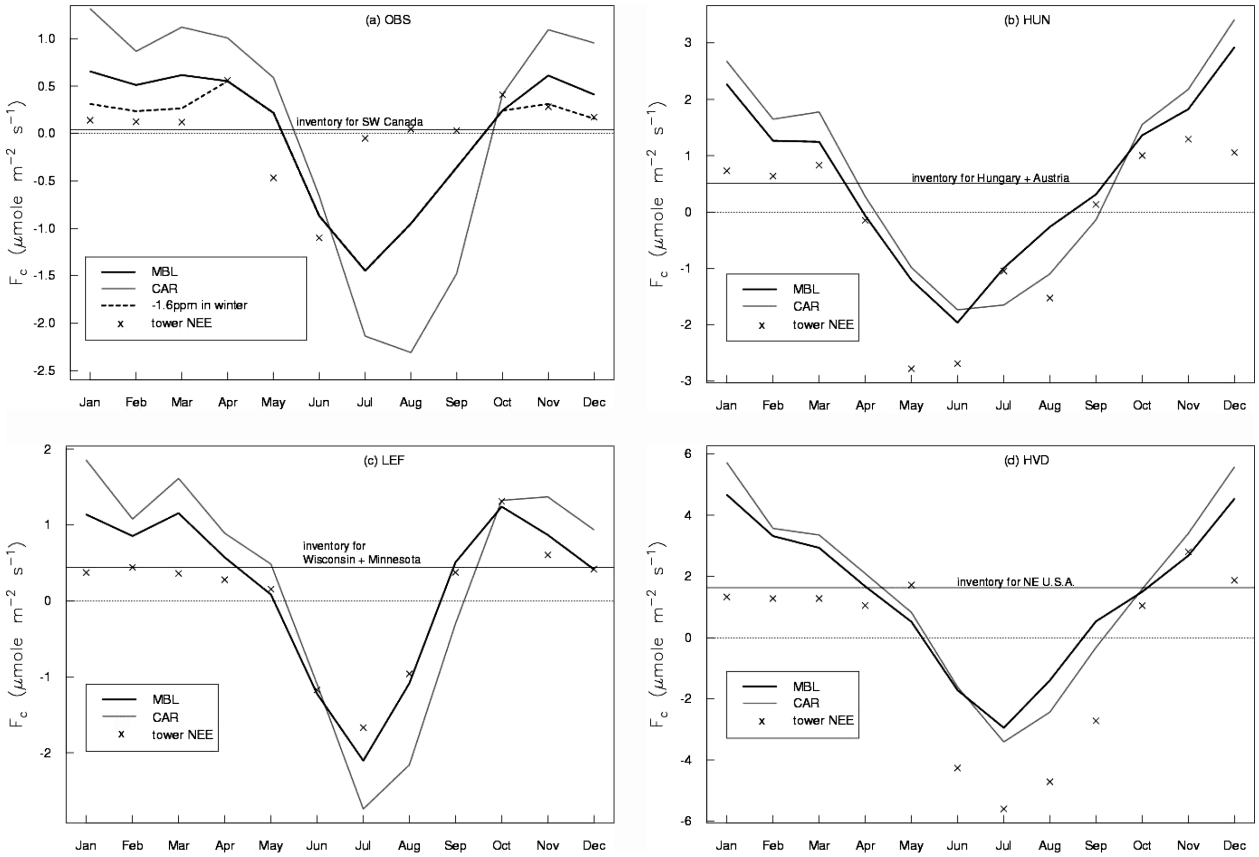

Fig 3. Regional CO_2 flux estimates calculated as described in the text (lines), and local fluxes measured at the towers by eddy covariance methods (×): (a) OBS, (b) HUN, (c) LEF and (d) HVD. CO_2 in the free troposphere over the towers was estimated either from MBL data (black line) or aircraft data from 5 km over Colorado (CAR, grey line). Thin horizontal lines indicate inventory estimates of fossil fuel emissions of CO_2 for the regions indicated. At OBS the calculation was repeated with wintertime (November–March) ΔC values reduced by 1.6 ppm to account approximately for pollution from thousands of kilometres distant (dotted line, see text).

expectations. The regional landscape around OBS is a patchwork of forest stands of varying ages, with fire as the main disturbance, and the stand in the immediate vicinity of the tower is relatively old, having last burned about 120 yr ago. Younger stands are more productive (Litvak et al., 2003), and our regional flux estimate probably reflects the influence of these younger stands on a large spatial scale. Similarly, the vegetation in the immediate vicinity of HVD is a protected and managed aggrading hardwood forest, while the surrounding area includes less productive forests, agricultural fields and human developments, all of which are likely to take up less carbon during the growing season.

Figure 3 shows a single year of data for each tower, but examination of other years for LEF, HVD and OBS gave very similar results (only one full year of NEE data was available from HUN).

Our regional flux estimates are consistently much greater than local NEE at all the towers in winter (Fig. 3). It is likely that emissions of CO_2 from fossil-fuel combustion within the larger area of the regional estimates contribute to this discrepancy. The towers are located to minimize the contribution of anthropogenic emissions on measurements of NEE. To estimate the magnitude of the anthropogenic CO_2 flux that contributes to F_C^0 we used measurements of CO and SF_6. Carbon monoxide is emitted during burning, and CO/CO_2 emission ratios are reasonably well known for industrialized areas. To estimate anthropogenic emissions of CO_2 from CO data we used an emissions ratio of 20 parts per billion (ppb) of CO per ppm of CO_2, which is appropriate for North America and Western Europe (Bakwin et al., 1998b). There are no known natural sources of SF_6, which is used primarily as a dielectric insulator for industrial applications. Hence, SF_6 is a good tracer for industrial activities. We calculated a CO_2/SF_6 emissions ratio of 15.3 ppm/ppt (parts per trillion) from global emissions inventories. Several trace gas species including CO and SF_6 are measured in flask samples collected weekly at all sites of the NOAA/CMDL Cooperative Air Sampling Network, which includes LEF and HUN. At HVD CO was measured using a continuous, *in situ* analyser (J. W. Munger, Harvard University, unpublished data), but SF_6 was not measured. No SF_6 or CO data were available from OBS.

Regional estimates of the anthropogenic flux of CO_2 were calculated from SF_6 and CO using eq. (5) and using MBL data

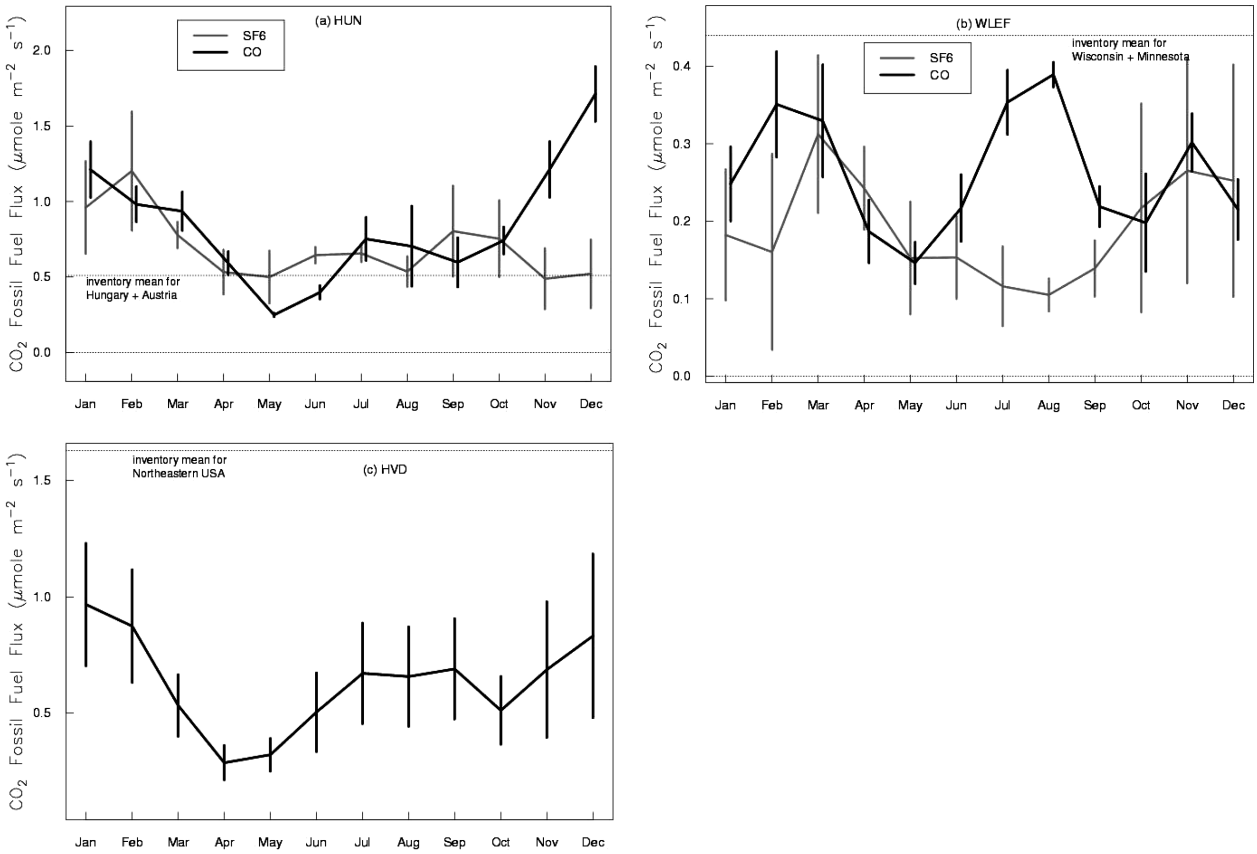

Fig 4. Regional fossil fuel flux of CO_2 estimated from CO and SF_6 data using the methods described in the text. Measurements of SF_6 at HUN (a) and LEF (b) were started in mid-1997. Data are averaged for 1998–2001 for HUN and LEF and for 1996–2001 for HVD (c), and error bars show one standard deviation of the mean across years. Annual mean fossil fuel emissions from inventory estimates (dashed horizontal lines) have been calculated for the regions indicated by multiplying the human population density by the national per capita emissions (Marland et al., 2002).

for these species from the NOAA/CMDL network (unpublished data). The method is identical to that used to compute CO_2 fluxes, F_C^0, and the results should be representative of the same regions as those for CO_2.

At HUN and LEF anthropogenic CO_2 fluxes calculated using CO and SF_6 are in good agreement, and agree fairly well with inventory estimates from these regions (Figs 4a and b). The anthropogenic flux calculated from CO at HUN shows a fairly strong seasonal cycle, with higher emissions in winter than summer. Anthropogenic emissions of CO_2 in Europe are expected to exhibit a similar seasonal cycle (Levin et al., 1995). Emissions of SF_6 are not known to be seasonal, so anthropogenic CO_2 emissions calculated from SF_6 would not be expected to be seasonal. Anthropogenic emissions of CO_2 are also seasonal in the USA, with higher fluxes in winter than summer (G. Marland, personal communication, 2003), but seasonal patterns calculated from CO at LEF and HVD are complex. In summertime it is likely that oxidation of biogenic hydrocarbons such as isoprene contributes to the abundance of CO at these towers (Potosnak et al., 1999), but this source is not considered in our analysis. Seasonal differences in transport may also contribute to the seasonal pattern of calculated anthropogenic fluxes, but examination of these seasonal changes is outside the scope of our simple one-dimensional analysis.

Our estimates of the anthropogenic CO_2 flux at HUN are in good agreement with the inventory estimate for Hungary and Austria (Fig. 4a). Other areas of Western Europe exhibit similar flux densities. At LEF our estimates based on CO and SF_6 are about half of the inventory value for the states of Wisconsin and Minnesota (Fig. 4b). The area influencing these calculations may be substantially larger than this, and regions farther from the tower in the prevailing westerly wind direction are generally of lower population density. For example, the population densities of North and South Dakota are 10–15% of those of Wisconsin and Minnesota. The calculated flux at HVD is also substantially lower than the inventory estimate for the Northeastern USA (New York and the New England states) (Fig. 4c), again suggesting that the area of influence for the tower mixing ratio data is substantially larger than this densely populated region.

We have no CO or SF_6 data from OBS. The region for several hundred kilometres around the tower is very sparsely populated. However, data from other high latitude sites in Canada indicate

that pollutants are elevated in the continental ABL in winter due to long-range transport from Europe and Asia. At both Alert (82.5°N, 62.5°W) and Fraserdale (49.9°N, 81.6°W) CH_4 is enhanced in winter by about 25 ppb relative to the high-latitude MBL (Worthy et al., 1998). Using a CH_4/CO_2 emissions ratio of 16 ppb/ppm from the AGASP III programme (Conway et al., 1993), this translates to an excess of 1.6 ppm of CO_2 in the continental ABL over Canada in winter and represents a contribution to the gradient of CO_2 that results from fluxes thousands of kilometres upwind of the tower. Subtracting this amount from $(C-C_{FT})$ at OBS gives results in reasonable agreement with the tower NEE in winter (Fig. 3a).

The magnitudes of our estimates of anthropogenic contributions to the regional CO_2 fluxes are in fair accord with those which are needed to explain the wintertime differences between F_C^0 and NEE at these sites (Fig. 3). Fossil-fuel emissions also affect our regional flux estimates in summer, especially at HVD which is in an area of particularly high fossil-fuel emissions density (Fig. 3d). In these temperate areas fossil-fuel fluxes are believed to be substantially higher in winter than summer (Levin et al., 1995; G. Marland, personal communication, 2003).

6. Discussion

Our budget analysis indicates that it is feasible to measure F_C^0 on a regional scale (i.e. $\sim 10^6$ km^2) by using measurements of CO_2 mixing ratios if horizontal and vertical advection can be estimated. The parametrization represented by eq. (2) is necessarily rough because at present sufficient data do not exist to enable a more accurate representation of horizontal and vertical advective exchange. This could be accomplished by using a mesoscale network of tower and aircraft sites at which CO_2 mixing ratios are accurately measured, and interpreting of the data with a trajectory model. The spacing of such a tower network should be of the order of several hundred kilometres, the approximate length scale represented by trace gas mixing ratio measurements (Gloor et al., 2001). Frequent vertical profiles over the towers using small aircraft would define the vertical mixing ratio difference between the ABL and FT. The trajectory model would provide observationally based estimates of wind vector (U and w in eq. 1), z_i and other parameters important for estimation of surface fluxes. An early study of this type, though mainly using data from a research aircraft campaign, has been presented by Gerbig et al. (2003).

Though data from very tall transmitter towers are least affected by very local surface exchange processes, our data for HVD, HUN and OBS indicate that properly selected measurements on short (30–115 m) towers also reflects regional scale processes. Small (0–2 ppm) daytime vertical gradients from the surface layer to the mid-ABL can be adequately estimated if surface exchange data are available (Potosnak et al., 1999; Davis et al., 2000), and these gradients are fairly small relative to the CO_2 difference across the top of the ABL, and to day-to-day changes in CO_2 that are associated mainly with synoptic variability.

The strategy outlined here also provides a means to assess regional anthropogenic fluxes of CO_2 by using specific tracers such as CO and SF_6. Hence, these tracers should be measured in any future tower and aircraft network and calibrations should be carefully tied to internationally accepted standards. Measurements of other tracers may provide greater specificity to particular anthropogenic processes.

Though there are dozens of towers worldwide where NEE is being measured, at only a very few of these sites are measurements of CO_2 mixing ratios traceable to the globally accepted WMO mole fraction scale. A relatively small increase in effort is required to calibrate CO_2 measurements adequately. Such an effort would yield an abundance of CO_2 mixing ratio data over continental areas that would be extremely useful to constrain estimates of regional net atmosphere/biosphere exchange of CO_2.

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