Regional Carbon Dioxide Fluxes from Mixing Ratio Data

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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 advection 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 continental and marine boundary layers. Therefore, as a first approximation we parameterize advection as a vertical exchange term related to the vertical gradient and the mean vertical velocity from NCEP Reanalysis. We then calculate the net surface exchange of CO$_2$ from CO$_2$ mixing ratio measurements at our tower sites. The results provide estimates of the surface exchange that are representative of a regional scale (i.e., $\approx 10^6$ km$^2$). Comparison to 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, separated by several hundred km, where CO$_2$ is accurately measured would provide data to estimate advection and hence provide a means to measure 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.
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 growing season length 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 (e.g., 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 program (Baldocchi et al., 2001), address NEE on rather 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 CO₂ exchange at the 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 CO₂ 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 CO₂ are clearly needed over the continents to improve estimates of regional net exchange of CO₂ 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 trace gas mixing ratio at a continental tower site by using measurements of the industrial solvent C₂Cl₄, demographic data as a proxy for the spatial distribution of C₂Cl₄ sources, and a trajectory model. They found that the tower measurements are sensitive to emissions over an area of roughly 10⁶ km². However, sources of C₂Cl₄ were mainly distant from the tower. Because of large proximate sources and sinks of CO₂ in terrestrial systems, CO₂ mixing ratios are extremely variable on short time scales near the ground. For example, a huge (tens of ppm) diurnal cycle typically exists during the growing season resulting from the covariation of biotic activity (net uptake of CO₂ during daytime, net loss of CO₂ from the biosphere at night) and atmospheric vertical mixing (deep during daytime, shallow at night) (Leith, 1963; Bakwin et al., 1998a).

We examine CO₂ mixing ratio and atmosphere/surface exchange data from four temperate, continental sites. For each site we construct a simple CO₂ budget for the lower atmosphere that includes surface exchange, a rate of change term, and horizontal and vertical advection. By approximating advection as primarily a vertical exchange we estimate the advection term at each tower site by using
an exchange time for air in the atmospheric boundary layer (ABL) that is derived from modeled 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 confidence that measurements of CO$_2$ mixing ratios on continental towers can be useful 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 to estimate 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 FLUXNET sites where NEE was also measured. The sites are the 447-m-tall LEF 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., 2003). Measurements of CO₂ 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 of the Chequamegon Ecosystem Atmosphere Study which focuses on understanding the factors controlling the net exchange of CO₂ of the regional forest ecosystems (see Global Change Biology special issue, 2003). 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 CO₂ mixing ratios and NEE have been made at HVD since 1990 (Wofsy et al., 1993; Goulden et al., 1996a; Goulden et al., 1996b), 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 analyzed 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 km²). The site and measurements are described by Haszpra et al.
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; 1999b; 2001).

The OBS site is an open-canopy boreal black spruce forest with an understory dominated by feather and sphagnum mosses. The landscape for many hundreds of km 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 75-80 years 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 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 typical synoptic events at LEF has been examined in detail (Hurwitz, M.D., Ricciuto, D.M., Davis, K.J., Wang, W., Yi, C., Butler, M.P. and Bakwin, P.S. Advection of carbon dioxide in the presence of storm systems over a northern Wisconsin forest. Submitted to J. Atmos. Sci.). 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 averages, which removes variability 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 appreciably change our results.

The budget of CO$_2$ in the ABL can be written as

$$\frac{∂C}{∂t} = \left(\frac{RT}{p}\right) \frac{F_c}{z_i} - \sum_i \left(\frac{∂C}{∂X_i}\right), \quad (1)$$

where $R$ is the universal gas constant (in units of Pa m$^3$ K$^{-1}$ mole$^{-1}$), $T$ is temperature (K), $p$ is pressure (Pa), $F_c$ is the net surface flux of CO$_2$ ($\mu$moles m$^{-2}$ s$^{-1}$), which includes both biogenic (NEE) and anthropogenic (fossil fuel) fluxes, $z_i$ is the average depth of the convectively mixed daytime ABL (m), $U_i$ is the wind speed (m s$^{-1}$) in each orthogonal direction, $X_i$, and $C$ is the molar mixing ratio ($\mu$mole CO$_2$ per mole dry air, ppm). The second term on the right-hand side represents horizontal and vertical advection, and we have ignored diffusion.

Equation 1 is derived from the conservation equation by Reynolds averaging followed by integration over the vertical dimension. A term representing the covariance of $F_c$ and $z_i$ has been ignored. Below we demonstrate that this term is probably relatively small in most cases.

Changes in trace gas mixing ratios at a site are influenced by processes occurring for a few hundred kilometers upwind (Gloor et al., 2001). Hence, Equation 1 provides a framework to estimate net surface fluxes ($F_c$) over a large region if advection of CO$_2$ can be measured. Limited existing data from above the ABL over the continent indicate that the vertical CO$_2$ difference between the ABL and FT is typically larger than the large scale horizontal gradients such as the difference between the FT over the continent and the marine boundary layer (Figure 1). Hence, as a first approximation advection in Equation 1 can be approximated by a term describing vertical exchange between the ABL and the FT:

$$U_i \left(\frac{∂C}{∂X_i}\right) \approx \langle w \rangle \Delta C / z_i, \quad (2)$$
where \( \langle \omega \rangle \) is the mean vertical velocity in the ABL and \( \Delta C \) is the mixing ratio difference between the ABL and the FT. The quantity \( \langle \omega \rangle / z_i \) represents the exchange rate for air in the ABL. If \( \langle \omega \rangle \) and \( \Delta C \) can be estimated then \( F_c \) can be calculated directly:

\[
F_c = \left( \frac{p}{RT} \right) \left( z_i \frac{\partial C}{\partial t} + \langle \omega \rangle \Delta C \right). 
\] (3)

For each tower site we estimate \( \langle \omega \rangle \) as the monthly mean of the absolute value of daily vertical velocity from the NCEP Reanalysis product (Kalnay et al., 1996), which we have converted from pressure coordinates (Pa/s). Resolved vertical velocity in the NCEP model balances horizontal divergence, and represents a grid-cell (about 200 × 200 km) average value. <Steve or Ken please help with more detail here!>

4. Measurements

Mixing ratios of CO\(_2\) were measured using non-dispersive infrared gas analyzers (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, Colorado, USA (Zhao et al., 1997). The data are reported as mole fractions relative to dry air (parts per million, 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 CO\(_2\) mixing ratio is observed in the atmospheric surface layer, the lowest several tens of meters 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; Bakwin et al., 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 hour) 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 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 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 (Figure 1), and had minimal effect on the results.

Monthly means of $\partial C/\partial t$ were computed from smooth curve fits (Figure 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).

To calculate $\Delta C$ we need measurements of CO$_2$ within and above the ABL at the tower sites. The tower data give a direct measure of CO$_2$ mixing ratio in the ABL (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, Colorado (NWR, since 1967), and aircraft flights over north-central Colorado (CAR, every 1-2 weeks since 1992) and over the HVD site (HFM, about one flight per month since 2000) (NOAA/CMDL, unpublished data). No long-term aircraft data were available from over Europe. Aircraft flights over LEF and HUN have begun
recently, but these 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 (Figure 1). Hence, lacking direct measurements in the FT over the towers during 1997 (LEF, HVD, OBS) and 1998-1999 (HUN), we use data from the MBL at the latitude of each tower and from 5 km altitude at CAR as proxies. Comparison of results using these two data sets to estimate CO$_2$ in the FT over the towers gives an idea of the uncertainty introduced into the calculation of $F_c$. A similar strategy was employed and discussed further by Helliker et al. (2003). 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).

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 to $\langle w \rangle \Delta C$ (Table 1), so our estimates of $F_c$ are only weakly dependent on $z_i$. 
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, 1998; Yi et al., 2001). Of course, $z_i$ also varies with 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 $F_c$ and $z_i$ are correlated on synoptic time scales, which would require an additional term in Equation 1. 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 $F_c$ equals -3 and -1 µmole m$^{-2}$ s$^{-1}$ as a 24 hour mean during these conditions. If fair and disturbed conditions occur with equal frequency then there is a covariance term of $+0.5$ µmole m$^{-2}$ s$^{-1}$, roughly half the magnitude of the value of $\langle w \rangle \Delta C$ in summer (Table 1). The true covariance will almost certainly be much smaller than this since disturbed conditions occur less than half the time, and since $F_c$ and $z_i$ are not perfectly correlated. In winter the biogenic component of $F_c$ (mainly soil respiration) probably responds weakly to synoptic conditions since soil temperatures change relatively slowly. Hence, using monthly mean values of $F_c$ and $z_i$ is a reasonable first approximation.

5. Results

At LEF, HVD and HUN 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 fall 1–2 months before the forest becomes a net source for CO$_2$ to the atmosphere (Figure 2). These patterns indicate that advection plays a role in the budget of CO$_2$ at these sites, at least during spring and fall. 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 3 allows us to use CO$_2$ mixing ratio measurements from tower sites to estimate the regional surface flux of CO$_2$, $F_c$, 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., $\approx 10^6$ km$^2$. At LEF and HUN $F_c$ is in reasonable accord with the local scale flux measured by eddy covariance (NEE) during the spring, summer and fall seasons (Figure 3b and 3c). Though the spatial scales represented by these two flux estimates are greatly 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 ($F_c$) indicates much more uptake by the vegetation than the local NEE (Figure 3a), while at HVD $F_c$ indicates somewhat less summertime uptake than the local NEE (Figure 3d). These results are in harmony with 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 75–80 years ago. Younger stands are more productive (Goulden ????), and our regional flux estimate likely reflects the influence of these younger stands at the large spatial scale. Similarly, the vegetation in the immediate vicinity of HVD is a protected and managed 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.
Values in Figure 4 are for a single year of data, 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 (Figure 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 $F_c$ 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 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 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 analyzer (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$_2$ at HUN and LEF calculated using CO and SF$_6$ are in good agreement, and agree fairly well with inventory estimates from these regions (Figure 4). 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
SF₆ would not be expected to be seasonal. Anthropogenic emissions of CO₂ are also seasonal in the U.S.A., with higher fluxes in winter than summer (G. Marland, personal communication, 2003), but we do not observe seasonality in the fluxes calculated from CO at LEF or HVD. Seasonal differences in transport may also contribute to the seasonal pattern of calculated anthropogenic fluxes. For example, there is a higher frequency of trajectories from the northwest at LEF and HVD in winter than in summer, and transport distances are generally greater in winter. Regions to the northwest of both towers are more sparsely populated than in other upwind sectors.

Our estimates of the anthropogenic CO₂ flux at HUN are in good agreement with the inventory estimate for Hungary and Austria. Other areas of Western Europe exhibit similar flux densities. At LEF our estimates based on CO and SF₆ are about half of the inventory value for the states of Wisconsin and Minnesota. 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. The calculated flux at HVD is also substantially lower than the inventory estimate for the northeastern U.S.A. (New York and the New England states), again suggesting that the area of influence for the tower mixing ratio data is substantially larger than the densely populated region.

We have no CO or SF₆ data from OBS. 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) CH₄ is enhanced in winter by about 25 ppb relative to the high-latitude MBL (Worthy et al., 1995). Using a CH₄/CO₂ emissions ratio of 16 ppb/ppm from the AGASP III program (Conway et al., 1993), this translates to an excess of 1.6 ppm of CO₂ in the continental ABL over Canada in winter and represents a contribution to the gradient of CO₂ that results from fluxes thousands of km upwind of the tower. Subtracting this
amount from ΔCO₂ at OBS gives results in reasonable agreement with the tower NEE (Figure 3a).

The magnitudes of our estimates of anthropogenic contributions to the regional CO₂ fluxes are in fair accord with those which are needed to explain the wintertime differences between \( F_c \) and NEE at these sites (Figure 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 (Figure 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 \( F_c \) on a regional scale (i.e., \( \approx 10^6 \text{ km}^2 \)) by using measurements of CO₂ mixing ratios if horizontal and vertical advection can be estimated. The parameterization represented by Equation 2 is necessarily rough because at present sufficient data do not exist to enable a more accurate representation of advective exchange. This could be accomplished by using a mesoscale network of tower and aircraft sites at which CO₂ mixing ratios are accurately measured, and interpretation of the data with a trajectory model. The spacing of such a tower network should be on the order of several hundred km, the approximate length scale represented by CO₂ 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 \( (U_i \text{ in Equation 1}) \). 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$_6$.

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 regional net atmosphere/biosphere exchange of CO$_2$.

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Figure Captions

Figure 1. Difference between CO$_2$ mixing ratio at various locations and the marine boundary layer 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, Colorado; CAR, aircraft data from 5 km over north-central Colorado; HFM, aircraft data from 4.5 km over Harvard Forest; MLO, the Mauna Loa Observatory in Hawaii (3.4 km altitude). MLO is included to give a measure of the vertical gradient over the ocean.

Figure 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 is 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 fit with a smooth curve (thick black line) after the method of Thoning et al. (1989). Gray lines are local NEE data (tower eddy fluxes) that have been smoothed with a running mean filter with a 5-day time constant for 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 marine boundary layer at the latitudes of the tower sites (GLOBALVIEW, 1999). Scales for each tower are identical.

Figure 3. Regional CO$_2$ flux estimates calculated as described in the text (lines), and local fluxes measured at the towers by eddy covariance methods (x). CO$_2$ in the free troposphere over the towers was estimated either from marine boundary layer data (MBL, black line) or aircraft data from 5 km over Colorado (CAR, gray 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) ΔCO₂ values reduced by 1.6 ppm to account approximately for pollution from thousands of km distant (dotted line, see text).

**Figure 4.** Regional fossil fuel flux of CO₂ calculated from CO and SF₆ data using the methods described in the text. Measurements of SF₆ at HUN and LEF were started in mid-1997. Data are averaged for 1998-2001 for HUN and LEF, and for 1996-2001 for HVD, 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).
Table 1. Monthly values of terms in Equation 3 at LEF (1997), and local NEE from the tower eddy fluxes. Units are µmoles m\(^{-2}\) s\(^{-1}\).

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<th>Month</th>
<th>(&lt;w&gt;\Delta C)</th>
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<th>(F_c)</th>
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Figure 2.
Figure 3a.
Figure 3b.
Figure 3c.
Figure 3d.
Figure 4a.
Figure 4b.
Figure 4c.