Transport of Carbon Dioxide in the Presence of Storm Systems over a Northern Wisconsin Forest

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ABSTRACT
Mixing ratios of CO₂ often change abruptly in the presence of inclement weather and low pressure systems. Water vapor mixing ratio, temperature, wind speed, and wind direction data are used to infer that the abrupt changes in CO₂ mixing ratios at a site in northern Wisconsin are due to tropospheric mixing, horizontal transport, or a combination of both processes. Four different scenarios are examined: the passage of a summer cold front, a summer convective storm, an early spring frontal passage, and a late autumn low pressure system. Each event caused CO₂ mixing ratios to change rapidly when compared to biological processes. In one summer convective event, vertical mixing caused CO₂ mixing ratios to rise more than 22 ppm in just 90 s. Synoptic-scale transport was also evident in the presence of storm systems and frontal boundaries. In the cases examined, synoptic-scale transport changed CO₂ mixing ratios as much as 15 ppm in a 1-h time period. The events selected here represent extremes in the rate of change of boundary layer CO₂ mixing ratios, excluding the commonly observed venting of a shallow, stable boundary layer. The rapid changes in CO₂ mixing ratios that were observed imply that large mixing ratio gradients must exist, often over rather small spatial scales, in the troposphere over North America. These rapid changes may be utilized in inverse modeling techniques aimed at identifying sources and sinks of CO₂ on regional to continental scales.

1. Introduction

The mixing ratios of atmospheric CO₂, a greenhouse gas, have been increasing globally at the average rate of 1.5 ppm yr⁻¹ for the past several decades (Conway et al. 1994). The major contributing factors to this long-term increase are fossil fuel combustion and land use change (Houghton et al. 1999). Emissions from these sources totaled roughly 7 GtC yr⁻¹ in the 1990s (Houghton et al. 2001). However, not all fossil fuel emissions remain in the atmosphere; a significant fraction of fossil fuel emissions are absorbed by the ocean and terrestrial biosphere. Because future climate change is highly dependent on CO₂ mixing ratios, it is important to understand the locations and the mechanisms of terrestrial and oceanic sinks.

Current methods of studying earth–atmosphere CO₂ fluxes tend to focus on either very large or small spatial scales. One approach uses temporal and spatial patterns in atmospheric mixing ratios of CO₂ to infer surface–atmosphere fluxes. Inverse studies (e.g., Tans et al. 1990) are an example of this approach. Such methods are useful for determining fluxes integrated over hemispheric to global scales. Continental-scale fluxes and the processes governing fluxes, however, are difficult to discern, partly due to a lack of continental data (Gurney et al. 2002; Rayner et al. 1999; Fan et al. 1998). Another method is to observe CO₂ fluxes directly using the eddy covariance technique. Over 100 eddy covariance flux towers recently have been established in a variety of ecosystems to provide continuous observations of the net ecosystem–atmosphere exchange (NEE), or surface flux, of CO₂ (Baldocchi et al. 2001). However, the representative integrated area of these NEE measurements is on the order of only several square kilometers. There-
fore, regional- to continental-scale fluxes are difficult to obtain through either type of method.

One way to improve the current estimates of regional- to continental-scale fluxes is to improve the spatial and temporal resolution of accurate CO₂ mixing ratio measurements available for use in inverse modeling studies. An understanding of the degree of variation in CO₂ mixing ratios in the continental ABL in space and time will aid in the design of observational networks used to determine regional to continental CO₂ budgets. Quantifying regional to continental CO₂ budgets at synoptic to seasonal time scales will require a synthesis of measurements and models of ecophysiological processes, boundary layer dynamics, and synoptic meteorology. This paper examines changes in CO₂ mixing ratio associated with synoptic weather systems.

2. Background

In midlatitude forests, surface fluxes of CO₂ exhibit strong diurnal and seasonal cycles resulting from the biological processes of respiration and photosynthesis combined with changes in advective mixing in the atmosphere. Both the biological and physical processes are driven by the diurnal and seasonal cycles of solar radiation. To illustrate the effects of these surface fluxes on boundary layer CO₂ mixing ratios, a typical diurnal cycle of CO₂ mixing ratios observed at the Wisconsin WLEF TV tower at three levels is shown in Fig. 1. During the nighttime, CO₂ is not well mixed from 11 to 396 m. High mixing ratios, sometimes greater than 500 ppm at 11 m, build up during the night within the stable boundary layer due to respiration of CO₂ from soil microbes and plants, but change little above this layer. After sunrise, CO₂ becomes well mixed as the convective boundary layer develops, and decreases slowly as photosynthesis exceeds respiration and net uptake of CO₂ occurs. Although daytime net uptake of CO₂ is generally the same order of magnitude as nighttime respiratory fluxes, CO₂ mixing ratios change more slowly during the daytime because the surface fluxes are acting upon a deeper, well-mixed convective boundary layer (Bakwin et al. 1998; Yi et al. 2001; Davis et al. 2003).

Seasonally, variations in mean CO₂ mixing ratios in the continental ABL are about 20 ppm against a background of about 375 ppm (Bakwin et al. 1998). During the growing season (late May–early September), daily average NEE is generally negative, meaning that CO₂ is taken out of the atmosphere due to photosynthesis. During the rest of the year, NEE is positive because of respiration of CO₂ into the atmosphere. Trends in CO₂ mixing ratios measured in the boundary layer at the tower exhibit a similar seasonal cycle. However, there are several periods during the year in which the sign of NEE does not match the trend in CO₂ mixing ratios (e.g., the surface flux is negative, but boundary layer CO₂ mixing ratios are increasing). This means that the NEE alone cannot account for the observed CO₂ mixing ratios; there must be horizontal and/or vertical transport of CO₂ at these times. Davis et al. (2003) show that, in fact, transport must be an important component of the continental CO₂ budget at all times of the year.

Figure 2 illustrates the annual cycle of NEE, CO₂ mixing ratios observed at WLEF in the boundary layer (396 m), and the free troposphere above 7000 m above sea level as observed by aircraft flights near Carr, Colorado, in 1998. We assume that free troposphere CO₂ mixing ratios at WLEF are similar those in Carr, Colorado, because 1) the zonal transport is rapid at these levels and 2) the free troposphere is farther removed from CO₂ sources and sinks, which are all at the surface. During February, it is evident that while cumulative NEE is increasing, indicating net respiration of CO₂ into the atmosphere, CO₂ mixing ratios are decreasing. During this same time, CO₂ mixing ratios are lower in the free troposphere than at 396 m, which means that vertical mixing of free troposphere air into boundary layer
air would cause CO₂ mixing ratios to decrease. The opposite situation occurs during July; cumulative NEE is relatively constant, while CO₂ mixing ratios are increasing. Carbon dioxide mixing ratios are higher in the free troposphere at this time, meaning that vertical mixing may be at least partially responsible for increasing boundary layer CO₂ mixing ratios. Synoptic events are in part responsible for this mixing.

Strong evidence also exists for horizontal CO₂ transport. Horizontal gradients of CO₂ exist both zonally and meridionally in the atmospheric boundary layer, much as they exist with other meteorological scalar variables such as water vapor and temperature. Such gradients are caused by uneven distributions of CO₂ sources and sinks. For example, boundary layer CO₂ mixing ratios in a highly productive forest during the growing season will be lower than those over a desert. Near WLEF, horizontal gradients may be induced by the presence of Lake Superior to the north or by fossil fuel burning in populated areas to the south and east. It will be shown that CO₂ gradients also exist between synoptic-scale air masses.

Events in which synoptic transport of CO₂ are examined may be useful in assessing horizontal CO₂ gradients that exist across North America. Figure 3 compares 5-day average daytime CO₂ mixing ratios at WLEF (45°55′N, 90°10′W) with CO₂ mixing ratios at the Northern Old Black Spruce site (NOBS; 55°53′N, 98°29′W) in Manitoba (Goulden et al. 1997). What is particularly interesting from this plot is that the difference between CO₂ mixing ratio values at the two sites depends on the time of the year. In the winter and fall of 1998, NOBS had a lower CO₂ mixing ratio than WLEF. Photosynthesis does not occur at either location in the winter, but greater rates of respiration and anthropogenic emissions in the region around the WLEF tower may increase the CO₂ mixing ratios there during the winter. Similarly, CO₂ mixing ratios at WLEF were lower than at NOBS during the spring and summer of 1998. These differences likely reflect continental-scale north–south gradients of CO₂ that are driven by latitudinal differences in respiration, photosynthesis, and fossil fuel combustion.

We hypothesize that both vertical transport from the free troposphere and horizontal transport are important in modulating the boundary layer CO₂ mixing ratios at WLEF during all seasons. Furthermore, a fraction of this transport takes place in abrupt events that are often concurrent with the passage of fronts or other synoptic features. Evidence supporting this hypothesis is presented in four case studies below in which rapid transport of CO₂ occurs: the passage of a summer cold front, a summer convective storm, an early spring frontal passage, and a late autumn low pressure system. Figure 4 presents synoptic maps that illustrate the meteorological conditions in the upper Midwest for each of the four events. These case studies show extreme examples of CO₂ transport. A climatology of such transport events is a logical goal for future study, as is the establishment of a continental network of CO₂ measurements.

3. Study site and methods

The study site is the 447-m-tall WLEF TV tower (in the Chequamegon National Forest, 14 km east of Park Falls, Wisconsin). This site is part of the AmeriFlux tower network, as well as the Chequamegon Ecosystem–Atmosphere Study (ChEAS). Mixing ratios of CO₂ are observed with high precision and accuracy at 11, 30, 76, 122, 244, and 396 m above the ground (Bakwin et al. 1998). Temperature, wind, water vapor mixing ratio, and turbulent fluxes of CO₂, momentum, latent heat, and sensible heat are measured at 30, 122, and 396 m (Davis et al. 2003).

The high-accuracy CO₂ data are available every 12 min at each level, and these data are used to calibrate 5-Hz LiCor data that are used to compute turbulent fluxes of CO₂ (Berger et al. 2001). These fast response data are necessary to capture the rapid nature of some of the CO₂ mixing ratio changes, which are as extreme as 22 ppm in 90 s. Temperature, water vapor mixing ratio, and wind data are also available at 5-Hz resolution. However, because of the turbulent nature of the 5-Hz signals, we present 5-min-averaged data in our analysis. Because of occasional instrument failure at certain levels, we interpret data from varying levels, depending on data availability.

During the events examined in this paper, rapid changes in CO₂ mixing ratio were coincident with changes in temperature and water vapor. The changes occurred at all observation heights, making it probable that these events encompassed the entire depth of the ABL. This also means that instrumental error is an unlikely source of the abrupt CO₂ changes. Surface fluxes are shown to be too small to produce the observed abrupt
changes in all four case studies. Thus, these events are caused by either vertical or horizontal transport of CO₂.

4. Results and analysis
a. 14 July 1998: Summer cold front

On 14 July 1998, a dry cold front passed through the WLEF region at about 1645 LST (Fig. 4). This frontal passage is indicated on Fig. 5 by a sudden wind shift from southwest to north, as well as rapid drops in both temperature and H₂O mixing ratio. Substantial down-drafts with 5-min-averaged vertical velocities between −0.5 and −1.0 m s⁻¹ were also observed concurrently with sharply higher surface wind speeds, indicating that air from the free troposphere may have mixed down to the surface. At the same time, the CO₂ mixing ratio at 30 m above ground level rose more than 22 ppm in only 90 s. Similar rapid increases were also observed at 122 m and 396 m (Fig. 5).

Before the frontal passage, it is likely that advection of CO₂ occurs as a result of southerly flow. Carbon dioxide mixing ratios decrease by about 15 ppm between 1300 and 1600 LST. Without transport, the surface flux required to cause this decrease over a typical boundary layer depth of 1500 m is roughly −90 μmol m⁻² s⁻¹. However, the observed average value of NEE during this time is only −12 μmol m⁻² s⁻¹; therefore, the observed decrease is not due to biological processes alone. This implies that a meridional gradient of CO₂ exists in which CO₂ increases with latitude. This gradient may
be forced by more productive forests and agriculture to the south of the WLEF site.

At the time of the frontal passage, advection of air with low CO$_2$ mixing ratios from the south ceases as the wind shifts to a northerly direction. Clearly, surface fluxes alone cannot explain the increase of 22 ppm in 90 s; the surface flux required to cause this increase over a 1500-m mixed layer is $10^4$ \text{mol m}^{-2} \text{s}^{-1}$. 

Fig. 5. Atmospheric changes at the WLEF tower on 14 Jul 1998 during a frontal passage. The frontal passage occurred at 1645 LST. All data shown were recorded at the 30-m level except for CO$_2$, for which 122- and 396-m data are also shown. Data are 5-min averages.
The observed NEE of $-12 \, \mu \text{mol m}^{-2} \text{s}^{-1}$ is too small and not even the correct sign. This event must be caused by vertical or horizontal transport. Although the evidence for deep vertical mixing is strong, as boundary layer CO$_2$ values approach free tropospheric values during a strong downdraft and temperature drop, horizontal transport cannot be completely ruled out.

b. 25–26 July 2000: Summer squall ahead of a cold front

On 25 July 2000, a dramatic rise in CO$_2$ was observed at WLEF at 2200 LST, about 15 h prior to the passage of a trough (Figs. 4 and 6). At this time, a strong squall line moved over the tower, producing 10 mm of rainfall and causing CO$_2$ mixing ratios to rise suddenly by over 15 ppm. This event differs from the 14 July 1998 event because it is not an actual frontal passage, and because it occurs at night, at which time a stable layer exists. Although CO$_2$ mixing ratios briefly converge at all tower levels during the squall passage, stable stratification is evident both before and after this event.

A temporary wind shift, temperature drop, and CO$_2$ increase occurred concurrently with this squall passage between 2200 and 2300 LST. It is likely that this is a case in which the horizontal transport of vertically wellmixed air occurred. As with the 14 July 1998 event, surface fluxes may be ruled out as the cause of the sudden rise in CO$_2$. Observed values of NEE at the time of the event were about 10 $\mu \text{mol m}^{-2} \text{s}^{-1}$. Although a sustained NEE of 10 $\mu \text{mol m}^{-2} \text{s}^{-1}$ may have produced very high mixing ratios of CO$_2$ near the ground in a stable nighttime layer, we observed that CO$_2$ increased sharply at all levels. The reported value of NEE was insufficient to cause the observed rise in CO$_2$ through the depth of this layer. Although vertical velocity values at WLEF did not show any sustained, vigorous downdrafts during the squall, this air may have been transported by westerly winds associated with the squall. These westerly winds initially reached speeds of 15 m s$^{-1}$ and were accompanied by a drop in the water vapor mixing ratio. The vertical mixing transported upper-level westerlies to the surface as well as CO$_2$. The CO$_2$ mixing ratio at 396 m, which was above the nocturnal stable layer, remained unchanged for several hours after 2300 LST. Subsequently, we observed modification, presumably by a combination of biological fluxes and advection. Water vapor mixing ratios also climbed to the presquall levels, but temperature remained fairly constant.

At the Willow Creek tower, 25 km southeast of WLEF, the squall passed almost 30 min after moving through WLEF. The Willow Creek CO$_2$ sensor at 30 m, which is calibrated using methods similar to those used at WLEF, registered a similar jump in CO$_2$ (Fig. 7), illustrating that this abrupt change in CO$_2$ was not of local origin but caused by the advection of a gradient in CO$_2$ mixing ratios.

The CO$_2$ mixing ratio continued to increase to nearly 375 ppm at 30 m at both towers after the squall passage. A stable nocturnal boundary layer reformed, and subsequent increases in CO$_2$ near the ground were probably due to respiration in the stable nighttime layer. We determined the CO$_2$ mixing ratio change brought by the squall passage by looking at data from higher levels that were not influenced by the stable layer (Fig. 6). Carbon dioxide mixing ratios at 30, 122, and 396 m at WLEF were relatively consistent at 362 ppm immediately after the squall passage. Data from Carr, Colorado, indicated that CO$_2$ mixing ratios in the free troposphere were around 370 ppm in late July 2000, close to those observed at WLEF after passage of the squall. We might expect that the CO$_2$ mixing ratio at WLEF after the squall passage was lower than in the free troposphere over Colorado because deep vertical mixing caused tropospheric air to mix with ABL air, which initially had mixing ratios of CO$_2$ as low as 340 ppm.

c. 28 March 1998: Spring cold front

There were three distinct events of interest on 28 March 1998, including the passage of a strong spring cold front at 1000 LST (Figs. 4 and 8). First, at 0400 LST, there was a rapid drop in CO$_2$ mixing ratios at all levels on the tower that is not directly associated with the cold front. This drop was not a result of mixing in the convective boundary layer because it occurred prior to sunrise. The second event involved a rise in CO$_2$ near 1000 LST and was a direct result of the frontal passage. Finally, the third event is a large decrease in CO$_2$ near 1100–1500 LST. The magnitudes of hourly NEE values are generally less than 1 $\mu \text{mol m}^{-2} \text{s}^{-1}$ throughout the day, so the surface fluxes were not responsible for any of the observed boundary layer CO$_2$ fluctuations.

Although no precipitation was recorded at the time of the first event, a small decrease in the water vapor mixing ratio and temperature was associated with the decrease in CO$_2$ mixing ratio at 0400 LST. Carbon dioxide mixing ratios in the free troposphere at this time of year are about 368 ppm (Fig. 2). At 0400 LST, CO$_2$ mixing ratios at 396 m fell to about 371 ppm. We expect that after this vertical mixing event, CO$_2$ mixing ratios at the tower would be slightly higher than in the free troposphere air because air from the free troposphere will entrain surface and boundary layer air, which have higher CO$_2$ mixing ratios in late March due to ecosystem respiration and fossil fuel combustion. There was no evidence of a sustained downdraft, however, and changes in temperature and water vapor mixing ratio were small and gradual. If the mixing event were due to entrainment of free troposphere air through deep vertical mixing, we might have expected a more dramatic decline in temperature and water vapor mixing ratio.

A more likely explanation of the change in CO$_2$ at 0400 LST is shallow vertical mixing. Prior to 0400 LST, CO$_2$ mixing ratios at 122 and 396 m increased to nearly
Fig. 6. Atmospheric changes at the WLEF tower on 26 Jul 2000 during the passage of a squall line. The squall passage occurred at about 2300 LST. All data shown were recorded at the 122-m level except for CO₂, for which 30- and 396-m data are also shown. Data are 5-min averages.

380 ppm. This indicates that the nocturnal boundary layer was deeper than 396 m. At 0400 LST, CO₂ mixing ratios fell simultaneously at all levels to about 371 ppm. Although this value was near the mixing ratio of the free troposphere, it was also about the CO₂ mixing ratio that was present at 396 m between 0000 and 0200 LST. One possibility is that the nocturnal boundary layer exchanged air with the residual layer above. A shallow mixing event either at the tower site or upstream of the tower would mix boundary layer and residual layer air, but might not mix the much drier air of the free troposphere. Horizontal transport of preexisting CO₂ gra-
Both increased and decreased with increasing latitude.

North of WLEF, and there were regions in which CO2
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water vapor mixing ratios are not occurring. This im-
1400 LST because phenomena typically associated with
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layer height of 1000 m, a CO2 surface flux of
is followed by a gradual decrease of about 10 ppm at
westerly, but the initial increase in CO2 mixing ratios
increase, in CO2 mixing ratios. That deep tropospheric
advected into the WLEF region.
At the time of the cold front passage at about 1000
LST, winds shifted from the south-southwest to the
north-northwest, and both the temperature and the water
vapor mixing ratio dropped (Fig. 9). Mixing ratios of
CO2 increased by 13 ppm, ultimately reaching 385 ppm,
much higher than the free troposphere CO2 mixing ratios
of 368 ppm (Fig. 2). If this event represented vertical transport, we would have expected a decrease, not an
increase, in CO2 mixing ratios. That deep tropospheric mixing was not responsible for the increase in CO2 mixing ratios was further corroborated by the observed vertical CO2 gradient of 10 ppm between 30 and 396 m.
Therefore, we assume the frontal passage was associated with transport of CO2-rich air from the north-northwest.
After the frontal passage, winds remain north-northwestly, but the initial increase in CO2 mixing ratios is followed by a gradual decrease of about 10 ppm at all three tower levels between 1100 and 1400 LST. If we assume a typical late morning atmospheric boundary layer height of 1000 m, a CO2 surface flux of $-40 \mu\text{mol m}^{-2} \text{s}^{-1}$ would have been required for such a drastic change in CO2 mixing ratios. This is much larger than the measured surface CO2 surface fluxes of $-1 \mu\text{mol m}^{-2} \text{s}^{-1}$. We assume horizontal transport is responsible for the change in CO2 mixing ratios between 1100 and 1400 LST because phenomena typically associated with vertical transport, including decreasing temperature and water vapor mixing ratios are not occurring. This implied the gradient of CO2 was not continuous to the north of WLEF, and there were regions in which CO2 both increased and decreased with increasing latitude.

d. 10 November 1998: Movement of a low pressure center over WLEF

On 10 November 1998, CO2 decreased by about 9 ppm, then rebounded in a 2-h period in the presence of a vigorous low pressure system that passed 50–100 km to the north of WLEF (Figs. 4 and 9). Sea level pressure values at the center of the low dipped to nearly 967 mb as the low passed by the tower. At the tower, winds shifted from east-southeast to south-southwest between 1000 and 1200 LST. Biological phenomena did not produce such a rapid change in CO2; assuming an ABL height of 1.5 km, a mean surface flux of nearly 133 $\mu\text{mol m}^{-2} \text{s}^{-1}$ would have been necessary. Maximum observed values of NEE on 10 November 1998 were about 3 $\mu\text{mol m}^{-2} \text{s}^{-1}$.

Between 0600 and 1000 LST, CO2 mixing ratios increased from 377 to 383 ppm due to easterly winds, implying the existence of a zonal CO2 gradient. The abrupt drop in CO2 that occurred at about 1045 LST was associated with the beginning of a wind shift to a southerly direction. Carbon dioxide mixing ratios measured from flights over Carr, Colorado, indicated that the CO2 mixing ratio values in the free troposphere were about 366 ppm, making it possible that vertical mixing could have caused ABL CO2 mixing ratios to drop. However, a rapid decline in CO2 mixing ratio at 1045 LST corresponded with a 2°C increase in temperature, as well as a small increase in water vapor mixing ratio. If the abrupt changes in CO2 mixing ratios were due to deep tropospheric mixing, we would have expected the temperature and water vapor to decrease, similar to the deep mixing event presented in Fig. 5. We did not observe any periods of sustained negative vertical velocity near the time of the decreasing CO2 mixing ratios, further corroborating that the abrupt change of CO2 was not caused by proximal vertical transport.

A warm, moist air mass was horizontally advected into the region of WLEF as the low pressure system moved to the north of WLEF. This warm air mass was associated with a rapid decrease in CO2 mixing ratios. The rebounding CO2 mixing ratios from 1130 to 1230 LST corresponded to decreases in temperature and water vapor mixing ratio after the passage of an occluded front. The air mass that replaced the warm, moist air mass was different from the air mass prior to arrival of the moist air, as both water vapor mixing ratios and temperature were markedly lower at 1200 LST than at 1000 LST. Examination of data obtained at fixed points (such as towers) during periods of strong horizontal transport, like the event that occurred on 10 November 1998, may be utilized to further understand horizontal gradients in CO2 that exist across continental North America.

5. Discussion

The sparse network of CO2 measurements, insufficient model resolution, and a poor understanding of CO2
Fig. 8. Atmospheric changes at 30 m at the WLEF tower on 28 Mar 1998, in which horizontal and vertical transport phenomena are explored. All data shown were recorded at the 30-m level except for CO$_2$, for which 122- and 396-m data are also shown. Data are 5-min averages. Wind speed and direction data were not available before 0400 LST due to instrument failure.
transport prevent models from obtaining accurate regional- to continental-scale CO$_2$ fluxes. This paper identifies events in which synoptic transport and deep vertical mixing of CO$_2$ occur, and provides insight into the abrupt changes in CO$_2$ mixing ratios during these events. These large changes contain information about sources and sinks upwind of CO$_2$ measurement sites, and failure to resolve these large gradients of CO$_2$ would lead to inaccurate CO$_2$ surface flux estimates at small time scales.
Spatial gradients in CO₂ mixing ratios are caused by different surface fluxes resulting from differences in vegetation type and density. These gradients are modified by synoptic transport and are particularly large in the vicinity of frontal systems. The comparison between NOBS and WLEF for 1998, while only two points, supports a seasonal north–south gradient, though this gradient is not always reflected during the passage of frontal systems. This implies the existence of smaller-scale horizontal gradients in CO₂ mixing ratios.

For example, three cases of horizontal transport were identified in this paper. Prior to the passage of a strong summer cold front on 14 July 1998, a period of strong southerly winds was accompanied by a gradual decrease of CO₂ by about 15 ppm over a 3-h period. This event corroborates the north–south gradient inferred from Fig. 3, in which July CO₂ mixing ratios at NOBS are higher than those at WLEF. The spring cold front on 28 March 1998 was associated with a shift in wind direction from a southerly to a northerly wind. The wind shift was concurrent with the rapid change in CO₂ mixing ratios, and this event suggests that CO₂ mixing ratios increase to the north. Figure 3 shows that during late March, the gradient in CO₂ mixing ratios between NOBS and WLEF was small, and therefore smaller-scale gradients with a larger magnitude than that which is illustrated by Fig. 3 exist. Finally, the sign of the north–south gradient obtained with the passage of an occluded front on 10 November 1998 contradicts the gradient determined from Fig. 3. The passage of an occluded front on 10 November 1998 provides another illustration of horizontal CO₂ gradients that exist across North America. Prior to the occluded front passage, winds turned from an easterly to a southerly direction. This southerly flow was associated with a warming and a decrease in CO₂ mixing ratios, implying that air to the south of WLEF had lower CO₂ mixing ratios. As the occluded front passed, winds remained southerly, while the CO₂ mixing ratios rebounded. Though southerly winds were transporting this air over WLEF, the origin of the air mass behind the occluded front was likely to the north of WLEF, as the air was associated with low temperatures and low water vapor mixing ratios. Clearly, horizontal gradients in CO₂ exist that cannot be resolved by WLEF and NOBS.

6. Conclusions

Frontal systems and squalls are generally associated with synoptic transport of CO₂ and at times deep vertical mixing of CO₂ from the free troposphere to the surface. Carbon dioxide mixing ratios change rapidly in these situations. The rate of change of CO₂ mixing ratios excludes local biological exchange as the cause of the rapid transitions. Monitoring deep vertical mixing events at various towers that measure CO₂ will facilitate the determination of CO₂ mixing ratios in the free troposphere, even in the absence of direct free troposphere observations. Identification of synoptic transport of CO₂ across frontal systems allows us to examine the most dramatic horizontal gradients of CO₂. The existing sparse network of CO₂ measurements suggests transport-based explanations for some, but not all of the observed events. Future work will likely consist of a more thorough climatological examination of synoptic transport across frontal systems. Through these studies of CO₂ changes across frontal boundaries, we can start to develop a more thorough understanding of the horizontal and vertical CO₂ gradients that exist across North America. This understanding, in combination with a better CO₂ measurement network, will be useful for reducing errors in inverse model flux estimates.

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