### Measurements of Landscape-Scale Fluxes of Carbon Dioxide at

### Two AmeriFlux Sites Using a New Vertical Profiling Technique

by

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B.S., University of Alaska, 1998

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This thesis entitled: Measurements of Landscape-Scale Fluxes of Carbon Dioxide at Two AmeriFlux Sites Using a New Vertical Profiling Technique Written by Kristen Schulz has been approved for the Department of Chemistry and Biochemistry

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline

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Abstract

Carbon dioxide is the most significant greenhouse gas other than water vapor and because of its contribution to global warming there has been an intense effort over the past decade to understand the global carbon cycle. The terrestrial biosphere provides large sources and sinks for  $CO_2$  and thereby strongly affects the atmospheric burden and rate of change of  $CO_2$  mixing ratio. However attempts to account for the distribution of  $CO_2$  in the atmosphere have uncovered a "missing" sink, most likely located in mid-latitude forests. Quantifying this sink has been hindered by a lack of flux measurements over land and uncertainties in the methods available.

In this work, a new method for measuring vertical profiles of CO<sub>2</sub> within and above the atmospheric boundary layer was developed. It involves sampling into Tedlar<sup>®</sup> bags and analysis by non-dispersive infrared (NDIR) spectroscopy. This method was demonstrated to have a precision of 0.06% and accuracy of 0.04%.

The new method was used to measured  $CO_2$  profiles at two different sites; a forest near Park Falls, WI and a grassland site near Ponca City, OK. Both sites are located near  $CO_2$  flux towers, allowing intercomparison of the two methods. Both seasonal and regional variations in  $CO_2$  concentration were observed, with an average  $CO_2$  difference between spring and fall of 4.84±1.86 ppm in Ponca City and 6.23±1.52 ppm in Park Falls. Data collected during the field studies was used to calculate  $CO_2$  surface fluxes by a budget method. Calculated average daily surface fluxes during the summer were -0.38±0.18 ppm m/s and -0.17±0.08 ppm m/s in Park Falls and Ponca City respectively and 0.06±0.19 ppm m/s and -0.03±0.09 ppm m/s during fall. These results follow a general trend of increasing downward flux with increasing photosynthesis. Our surface fluxes were compared to the surface fluxes measured by eddy covariance at the nearby flux towers and the difference between the two is generally less than 0.3 ppm m/s.

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### Chapter 1: Introduction

## 1.1 Global Climate Change and CO<sub>2</sub>

Global climate change may arguably be the most important environmental issue of the  $21^{st}$  century. Scientists are now predicting a global surface increase of  $0.6 \,^{\circ}C \pm 0.2 \,^{\circ}C$  over the next century (IPCC 2001). The effects of this sort of temperature increase are: decreases in snow cover, glaciers and sea ice; increased sea level and ocean temperature, and increased frequency of extreme weather and El Nino events. It is still unclear how increased temperatures would affect crop production and ocean life.

The inevitability of rapid climate change has caused an increased interest in the global carbon cycle. Data from ice core samples indicate that the concentration of  $CO_2$  in the atmosphere had been stable at about 280 ppm from the last interglacial period (10,000 BP) until the start of the industrial revolution at the turn of the century (Taylor and Lloyd 1992; Smith, Cramer et al. 1993; Keeling 1995). Past observable changes in climate had corresponding changes in atmospheric  $CO_2$ . At the end of the last glaciation (a significant warming event), concentrations rose from 200 ppm in 17,000 BP (before the present time) to 280 ppm in 10,000 BP, causing an accumulation of 170 Gt of C at a rate of 0.01 ppm/yr (Sundquist 1991).

 $CO_2$ , although having a much lower global warming potential (GWP) than other greenhouse gases such as  $CH_4$ ,  $N_2O$ , and CFCs, exists in far greater concentrations and therefore has a substantial effect on the global radiation budget.  $CO_2$  is clearly a very important greenhouse gas, and what is more alarming is the observable and unprecedented increase in atmospheric  $CO_2$  in the last century from 280 ppm to nearly 380 ppm, estimated to be the highest concentration in the last 420,000 years (IPCC 2001). At its current rate of increase (1.5 ppm/yr), scientists predict  $CO_2$  concentrations to reach between 520 and 970 ppm by 2100 (IPCC 2001).

The rise in atmospheric  $CO_2$  can be primarily attributed to the combustion of fossil fuels (~75%) and changes in land use from tropical deforestation. Approximately half of the emitted  $CO_2$  remains in the atmosphere. Up until a few decades ago it was believed that oceans were responsible for the removal of the remaining emitted  $CO_2$ . Based on thermodynamics, the increase of 100 ppm in atmospheric  $CO_2$  should have caused a 1 µmol/L concentration increase in ocean surface water, (Toggweiler 1995). However new measurements and model predictions in 1990 indicated that oceans take up only between 26% and 44% of the excess carbon (Tans 1990); the rest is taken up by the terrestrial biosphere through photosynthesis and other biological processes.

Approximately 50% of initial carbon uptake is by photosynthesis, which is referred to as gross primary production (GPP)] (Steffen, Noble et al. 1993). The remaining half is referred to as net primary production (NPP), a fraction of which is shed as litter, incorporated into the soil, decomposed and emitted as CO<sub>2</sub>. Any remaining carbon, which is incorporated into the ecosystem as new plant growth is called net ecosystem production (NEP), some of which is lost during natural processes (fire, harvest, disease, etc.). The sum of all these processes is called net biome production (NBP). NBP is a small fraction of the initial carbon uptake and is

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the parameter necessary for determination of long-term (decadal) carbon storage. NBP varies greatly for each ecological system.

Much emphasis has been placed on forest ecosystems as they contain an estimated 86% of the world's above ground carbon (Olson 1983) and 73% of the carbon in soil (Post, Emanuel et al. 1982). Scientists estimate that 0.180 Gt C/yr is sequestered by temperate forest ecosystems (Sedjo 1993). (Bidsey, Plantinga et al. 1993) estimates that 31% of carbon sequestered in US forests is in live trees including roots, 59% in forest soils, 9% in litter, and 1% in other vegetation. Additionally, the size of timber stock in the United States increased by approximately 29% over the past 35 years (Sedjo 1993).

Agriculture also contributes to the carbon budget usually as land use changes. Approximately one fifth of the Earth's surface land is agricultural (Olson 1983), but this changes as population and farming technology changes. Conversion of forests to agricultural land results in a net positive  $CO_2$  flux. This was the major source of atmospheric  $CO_2$  before the industrial revolution with as much as 40 Gt of carbon released from 1750-1850 (Sundquist 1993) and still contributes to atmospheric carbon in developing nations.

Because most fossil fuel use occurs in the Northern Hemisphere and the mixing time between the hemispheres in on the order of one year, we expect to see a gradient between the Northern and Southern Hemispheres. Using information on known  $CO_2$  sources and sinks, models predict an interhemispheric gradient of 4-5 ppm; however, the measured gradient is only 3 ppm. This implies a "missing"  $CO_2$  sink at high latitudes in the Northern Hemisphere (Fan 1998). This northern

terrestrial sink has been estimated at anywhere from 0.3 Pg C year<sup>-1</sup> (Pacala, Holland et al. 2001) to 2.2 Pg C year<sup>-1</sup> (Fan 1998), but the size, spatial distribution and mechanisms are still poorly understood.

Current measurements have been insufficient to characterize this sink. Satellites can provide a good qualitative picture, but lack the required resolution of temporal CO<sub>2</sub> concentration changes. Aircraft campaigns provide only concentration measurements – not the desired fluxes – and are costly. The best method to date is ground-based tower measurement networks such as AmeriFlux (http://public.ornl.gov/ameriflux/Participants/Sites/Map/index.cfm) and FLUXNET (Running, Baldocchi et al. 1999). However, they are not always spatially representative of the region and the sites are widely spaced with small footprints.

Additionally, a possible bias in tower measurements was identified by (Denning, Collatz et al. 1996). The "rectifier" effect arises from the correlation between terrestrial sources and sinks, and the growth and mixing of the atmospheric boundary layer (ABL). The ABL is the lower-most layer of the atmosphere and exists as a deep, (up to 3 km) well-mixed layer during the day, collapsing at night into a shallow, poorly mixed layer. The primary terrestrial source of CO<sub>2</sub> is respiration by soil microbes and plants; the primary sink is photosynthesis. Photosynthesis has a larger effect on CO<sub>2</sub> concentration; therefore during the day photosynthesis dominates resulting in a net negative flux. A diurnal effect is observed where, at night microbes release CO<sub>2</sub> into the shallow nocturnal boundary layer and during the day, photosynthesis draws CO<sub>2</sub> down from a deep ABL. The end result is a nocturnal ABL that is greatly enriched in CO<sub>2</sub> compared to the free troposphere and a daytime ABL that is only slightly deficient. Thus, the surface concentration of terrestrial  $CO_2$  is, on average, greater than the rest of the atmosphere. A corresponding annual cycle is also observed between the spring and summer months when photosynthesis dominates and the fall and winter months when respiration dominates. The annual cycle contributes to 80% of the rectifier effect with the remaining 20% from the diurnal feature (Denning, Collatz et al. 1996).

Because land-based tower measurements are made mostly within the ABL, (the tallest tower is 400 m high) they may only be observing the seasonal and diurnal "rectifier" effect and not globally averaged  $CO_2$  changes. It is generally recognized that there needs to be more measurements made through the ABL and into the free troposphere.

#### 1.2 Bag Sampling Method

The need for more profiles of CO<sub>2</sub> through the ABL and into the free troposphere led us to develop a new method for sampling CO<sub>2</sub>. The most important aspect of measuring CO<sub>2</sub> profiles in the troposphere is to accurately measure the difference in concentration between the ABL and free troposphere, which can be as large as 20 ppm, but is most commonly 2-3 ppm. The method must therefore be able to measure CO<sub>2</sub> with an accuracy of  $\pm 0.2$  ppm. The most commonly used and most accurate method for measuring CO<sub>2</sub> is by non-dispersive infrared (NDIR) spectrometry; therefore we chose this analytical approach. The sampling method needed to be lightweight so that it could be used on a variety of platforms, such as balloons, kites and aircraft, with little operator skill. Previous methods of profiling involved either flying a NDIR instrument on a plane or sampling into glass flasks. The first method has the advantage of obtaining real-time, continuous profiles, but also requires rigorous pressure and temperature regulation, making it expensive and far too heavy for use on kites and balloons. Flask samples, because they are analyzed in a laboratory by NDIR, are both highly accurate and precise when collected without artifacts. However, any contamination to the flasks in the field or during transportation is not detected until they are analyzed, usually weeks after a mission has ended. We hoped to develop a method with the precision and accuracy of the flask sampling method but with the ability to analyze the samples in the field.

The method developed consisted of sampling air into 3-L Tedlar<sup>®</sup> bags for a period of 2 min at each altitude. Because the bags are filled and emptied at a constant ambient pressure, small, inexpensive air pumps can be used and the samples can be analyzed in the field by NDIR. Smaller, lighter pumps also mean the method can be used on a balloon or kite platform. Filling the bags over a period of 2 min provides a spatially averaged sample at each altitude. The method requires little operator skill; the pump is turned on before take off, constantly circulating air through the system to flush out tubing, and a simple rotary switch is used to switch between bags.

The bag sampling method was demonstrated to have a precision of 0.023 ppm and accuracy of 0.14 ppm. Tests were carried out to determine the diffusion of air into and out of the bag, and it was determined to be insignificant over the time scale of sampling and analysis.

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#### **1.3 Field Studies**

The new bag sampling method was used in six successful field missions to two different AmeriFlux sites: the WLEF tall tower in Park Falls, WI and near a flux tower in the vicinity of Ponca City, OK. Each site was visited during summer, spring and fall to ascertain both seasonal and regional variations in CO<sub>2</sub> profiles and fluxes. A total of 150 profiles were collected over a two-year period. The site's proximity to flux towers allowed us to compare our method to those used on the towers. The Wisconsin sampling site is located within the Chequamegon National Forest, approximately 10 km east of the town of Park Falls (population 2,790) and 1.7 km west of the 447-m WLEF television tower. The area is forested with a mix of northern hardwood, aspen, wetlands and small farms. The Oklahoma site is the Blackwell-Tonkawa airport, approximately 30 km northeast of Ponca City (population 25,919). The OK site is dominated by grasslands, agriculture (principally wheat) and cattle pastureland. The sites were chosen both for their proximity to flux towers and varied land uses.

Although the bag sampling method can be used for kite or balloon platforms, we opted to experiment with a new platform, a powered parachute (PPC). The PPC is an experimental, ultralight, manned aircraft. The PPC has a number of advantages over kites, balloons and even traditional aircraft. The US Federal Aviation Administration (FAA) greatly limits areas where kites and balloons can be used and requires the attachment of flags at every 50 ft of tether, making kite and balloon sampling difficult or impossible except in highly remote areas. As an ultralight, the PPC must follow the same flight guidelines as any aircraft flying by visual flight rules (VFR); however the pilot is not required to have a pilot's license. A well-trained and experienced pilot, however, is a must. As a manned aircraft, the PPC has more flexibility than kites or balloons to sample over specific terrain, but unlike traditional planes, it has a top speed of only 30 mph, making it safer for low altitude profiling. When weather conditions prohibited the use of the PPC, samples were acquired with a small airplane (Cessna 182). The only modifications to the method during aircraft flights were to sample only during the descent and to install a 5-cm diameter plastic tube from the air intake in the wing to the bag sampler to facilitate air flow around the bags. These measures prevented high concentrations of  $CO_2$  from aircraft engine exhaust from accumulating in the bag sampler.

In addition to  $CO_2$ , profiles were measured of temperature, pressure, water vapor, ozone. The basic meteorological parameters were used to determine the height and growth of the ABL. Water vapor and ozone measurements were useful as auxiliary data in evaluating the height of the boundary layer. Supplemental data including wind speed and direction, heading and GPS coordinates describe the landscape and weather conditions at the time of the profile.

#### 1.4 Flux Calculations

Monitoring concentrations of carbon dioxide are just one important aspect of the carbon cycle. Quantification of all sources and sinks are crucial and will become more so as the global community further commits to reducing their carbon emissions. The Kyoto protocol currently provides the option of carbon sequestration from reforestation or afforestration as a means to meet carbon reduction goals or for the purpose of trading "carbon credits" (Schulze, Valentini et al. 2002). For example, it's been estimated that slowing deforestation in just tropical latitudes can conserve up to 1.6 Pg of Carbon per year (Smith, Cramer et al. 1993). In order to meet their reduction goals, each country will need a full accounting of its carbon budget, as well as specific source/sink magnitudes and mechanisms. Any inconsistencies or inaccuracies will jeopardize the entire objective.

Historically, the terrestrial carbon sink was inferred from differences in atmospheric and oceanic models or changes in  ${}^{13}C/{}^{12}C$  ratios (Sundquist 1993), (Tans 1990), (Denning, Fung et al. 1995). This, however, can only provide an average for all land biota. Without knowledge of the mechanisms and magnitudes of sources and sinks for specific ecosystems it is impossible to estimate how changes in land use will affect the carbon budget. Therefore, direct measurements of fluxes in representative systems are needed.

Surface and entrainment fluxes are measured by basically three different techniques: chambers, micrometeorological methods and budgets. The method used depends on the desired spatial resolution of the measurement, budget constraints, and available tools.

Surface fluxes, characteristic of a type of soil or relatively homogeneous terrain, are generally obtained by a variety of chamber methods (Norman, Kucharik et al. 1997). The method and instrumentation is relatively simple. An enclosure is placed over a plant, leaf, soil sample or any other desired system, and the change in concentration of a scalar is measured over a period of time. The data can than be extrapolated over an entire ecosystem if extremely detailed information on the structure of the ecosystem is known. The method is simple and inexpensive and gives valuable information on base emission rates for a specific ecosystem component. Chamber methods do suffer from systematic uncertainties arising from the enclosures themselves.

Micrometeorological methods are the most common for long-term regional scale flux measurements, the most common being eddy covariance. The idea is to directly measure the flux as the average of the instantaneous product of the wind velocity and scalar density or mixing ratio (Dabberdt, Lenschow et al. 1993). Basic instrument requirements are a sonic anemometer to measure wind speed and direction and a fast CO<sub>2</sub> analyzer (most commonly a non-dispersive infrared spectrometer). Net ecosystem exchange can then be calculated by adding the eddy flux and carbon storage measurements (Goulden, Munger et al. 1996). Eddy covariance systems are frequently mounted on tall towers to increase the flux footprint and provide a long-term sampling platform (Berger, Davis et al. 2001), (Baldocchi, Falge et al. 2001), (Goulden, Munger et al. 1996). Data from a number of flux networks, such as AmeriFlux and FLUXNET, which are composed of dozens of flux towers throughout the world, are combined to estimate regional and global carbon storage.

The method we used was the boundary layer budget method (Denmead, Raupach et al. 1996), (Raupach, Denmead et al. 1992). This method treats the ABL as a well-mixed box whose volume is increasing throughout the day by entraining air from the free troposphere, which essentially dilutes the concentration of  $CO_2$  in the ABL. Therefore, fluxes can be calculated from measurements of the change in concentration in the ABL, change in the height of the ABL and concentration in the free troposphere. Budget methods are generally easy and inexpensive compared to eddy correlation methods, but do require highly precise and accurate measurements of  $CO_2$  within and above the ABL. In addition, the method assumes that the ABL is a well-mixed system and that the vertical velocity at the top of the ABL is less than the growth of the ABL. Therefore, the method works only under fair weather conditions.

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### Chapter 2: Development of Bag Sampling Method

#### 2.1 Motivation

Current approaches to understanding the carbon biogeochemical cycle range from land-based methods that derive information from studies of plant physiology, observations of changes in land use, and ecosystem modeling (Pacala, Holland et al. 2001) to atmosphere-based methods that compare long-term measurements of CO2 mixing ratios with predictions of global transport models using estimates of fluxes from known sources and sinks (Francey 1995). Local fluxes and CO<sub>2</sub> concentrations at heights up to 500 m are measured continuously at tall tower sites throughout the US (Bakwin and Tans 1995), (Berger, Davis et al. 2001), and a global network of flask sampling provides estimates of the global carbon budget (Fan 1998) but regional to continental scale fluxes are not quantified adequately by these approaches. The free troposphere, where CO<sub>2</sub> is relatively well mixed and not strongly affected by the diurnal cycle, is not sampled by this combination of towers or ground-level flask collections. Although fluxes are measured directly from towers using the eddy covariance method, the footprint characterized by the measurement is guite small (typically  $\leq 1 \text{ km}^2$ ).

Vertical profiling of CO<sub>2</sub> through the ABL provides free tropospheric values useful for estimating regional-to-continental scale fluxes using global transport models. Using the budget and/or gradient methods, vertical profiles through the boundary layer also may be used to derive landscape-scale fluxes of CO<sub>2</sub> having characteristic footprints of  $\approx 100$  km.<sup>2</sup> Therefore, it is highly desirable to have an inexpensive, highly portable method for vertical profiling of CO<sub>2</sub> through the ABL and well into the free troposphere. A new approach is described here for obtaining vertical profiles of CO<sub>2</sub> with high precision and accuracy. The method makes use of a powered parachute (PPC) as a sampling platform in combination with a new Tedlar<sup>™</sup> bag sampling technique.

#### 2.2 Current Vertical Profiling Methods

#### 2.2.1 Absorbance Detection

Carbon dioxide is a relatively simple gas to measure. It has strong absorbance bands in the IR in the frequency range 2030cm<sup>-1</sup> to 2240cm<sup>-1</sup> and is the second most abundant IR active gas (after water) in the atmosphere. Because of this, nondispersive infrared spectroscopy (NDIR) is by far the most common method for measuring CO<sub>2</sub> in the atmosphere. Highly accurate, fast and precise commercially available instruments are available. The vast majority of CO<sub>2</sub> measurements are based on this; however, IR absorbance is sensitive to changes in pressure, temperature and water vapor concentration (McDermitt, Welles et al. 1993). As a result, direct measurements of vertical profiles are difficult without rigorous correction methods (Daube Jr., Boering et al. 2002).

#### 2.2.1 Flask Network

One of the most common and simple methods for collecting and measuring CO<sub>2</sub> is by sampling into small evacuated glass flasks. The National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) has maintained a system of collecting samples in 2.5-L flasks at over 40 sites through the world for many years (www.cmdl.noaa.gov/ccgg/flask/index.html). Most of the long-term measurements we have of CO<sub>2</sub> were collected this way. Flasks are brought to the sampling site, evacuated, and then simply opened to collect the sample. This can be accomplished on a kite or balloon platform by employing a remote controlled solenoid valve (Kuck 1999). Alternately, samples can be collected from an aircraft, on which a small compressing air pump can be used to flush the flasks out, and then pressurize them with sample. This method decreases errors from contamination and samples over a larger altitude range (Matsueda and Inoue 1996). The flasks are then returned to a lab (often NOAA/CMDL) for analysis by NDIR with an analytical precision of 0.05 ppm (Cias, Tans et al. 1995).

The advantage to collecting a sample for analysis at the ground is that temperature and pressure are easily controlled in a laboratory setting. Also the method is simple and doesn't require a high degree of technical skill to collect the samples. Collecting a large sample of air also means one can measure other compounds in the air. CMDL routinely measures  $CH_4$ , CO,  $H_2$ ,  $N_2O$ ,  $SF_6$  and carbon isotope ratios, in addition to  $CO_2$ , in nearly all of its samples. Because the analysis is done in a lab, reproducibility, accuracy, and precision are excellent, and many samples can be analyzed in a single day.

There are disadvantages to flask collection. Filling an evacuated flask to atmospheric pressure takes only a fraction of a second and in so doing "grabs" whatever air is closest. This air may be comprised of higher or lower concentration air, caught in an eddy and therefore not characteristic of the concentration at that altitude. This problem is avoided when the sample is collected over a period of time with an air sampling pump as is used on aircraft platforms. Also, any errors in evacuating or filling or any contamination that occurred during transit and storage wouldn't be detected until the samples are analyzed, sometimes up to months after collection.

#### 2.2.2 Tower-based Measurements

Another method for measuring vertical profiles of  $CO_2$  is to set up a NDIR instrument on a tower (Bakwin and Tans 1995; Bakwin, Tans et al. 1998). Towers can be erected for this purposes or an existing television or radio tower can be used. The instrument is usually housed near the ground, inside a building, with inlet lines running up the tower to various altitudes. The same instrument may be used to measure CO<sub>2</sub> at different altitudes by switching valves to sample different sampling lines. This way, concentrations at a fixed place and altitude can be measured continuously for years. This provides extremely valuable information about diurnal and seasonal changes. In addition to mixing ratios, fluxes are usually measured directly via the eddy covariance method (Berger, Davis et al. 2001). However, tower measurements are limited to a fixed location, and, even for very tall towers such as the WLEF tower in Park Falls, WI which is 610 m tall, the majority of the measurements do not extend into the free troposphere, and the flux footprint is limited by the height of the tower.

# 2.2.3 Aircraft Methods

is open only during the time period that the hose is being filled

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In contrast to the tower based method, aircraft can be used as a platform to measure  $CO_2$  over large regions. Both NDIR and differential absorption lidar (DIAL) (Matson and Harris 1988) have been used, and direct measurements of fluxes by eddy covariance are common (Desjardins and MacPherson 1998). NDIR measurements on aircraft require corrections for pressure, temperature, air density, and flow distortions (Daube Jr., Boering et al. 2002). The instrumentation tends to be expensive, as are the aircraft usage fees (typically several hundred to a few thousand US dollars per hour). However, this provides invaluable information on the spatial variability of  $CO_2$  over large areas.

A new aircraft method is described here that makes use of a relatively inexpensive type of ultralight aircraft, a powered parachute (PPC) that can be operated in remote areas by individuals who do not hold a pilot's license. Samples are collected using a new Tedlar<sup>™</sup> bag sampling technique and analyzed at the ground within a short time after collection. This chapter characterizes and evaluates this new vertical profiling technique.

#### 2.3 Experimental Design and Materials

The bag sampling method consists of an aerodynamic polypropylene box containing twelve 3-L Tedlar<sup>™</sup> bags (SKC, Eighty Four, PA, Cat # 232-03) attached to a sampling manifold and small 12-V air pump (Gast, Bridgman, MI model 3D1060-101-1081). Figure 2.1 is a schematic diagram of the bag sampling system. Each bag is connected to a solenoid valve (Pneutronics, Hollis, NH, model 991-003063-012), which is open only during the time period that the bag is being filled. An is continuously anophic view is provide Ld. Telephic land Typerivisite from an inter put score the mass of the powered paracticle at a flow rate of 1 Linit. The anophed as parases therapph a glass fiber fitter (Gelman Glass Astrodisc<sup>10</sup>) to the interior particulate matter, dam through a 10-cm long, 1.0-cm i.d. polypropylene table filled with magnetism perchlorate followed by Driesie (calcum militic) to thy the



### Figure 2.1: Schematic diagram of the Tedlar<sup>™</sup>-bag sampling system.

where each flight, the bag sampler is removed and a second bag sample.

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#### emphotomator (LiCor, Lincoln, Nil, model L1-6252 or 21)

Air is continuously sampled via a ¼ in-o.d., 1/8-in i.d. Teflon<sup>TM</sup>-lined Tygon<sup>TM</sup> tube from an inlet just above the nose of the powered parachute at a flow rate of 1 L/min. The sampled air passes through a glass fiber filter (Gelman Glass Astrodisc<sup>TM</sup>) to remove particulate matter, then through a 10-cm long, 1.6-cm i.d. polypropylene tube filled with magnesium perchlorate followed by Drierite (calcium sulfate) to dry the air, and finally through the pump and into the manifold. When a bag is not being filled, air exits from the manifold through an open solenoid valve. To fill a bag, a 12position switch is set to open the solenoid to the desired bag, and a toggle switch is flipped to simultaneously power the solenoid valve to the bag and close the solenoid valve at the exit of the manifold. Thus, the manifold is flushed during periods when bags are not being filled. The 12-V PPC battery powers the entire sampling package.

Each bag is filled for two minutes over an approximate 300-m altitude range, with six bags filled on the ascent and six on the descent. Since the altitude range covered is generally 3 km or less, there is some overlap between the "up" and "down" samples. Also, samples are obtained over more than half of the approximately 50min flight so that the sampling procedure does a reasonably good job of averaging over atmospheric eddies. Alternating the location of "up" and "down" vertical profile samples provides both a test of homogeneity on the horizontal scale and a check of the analytical method.

After each flight, the bag sampler is removed and a second bag sampler installed on the PPC so that a new profile can be sampled while the first set of samples is being analyzed. Bags are analyzed using a nondispersive infrared (NDIR) spectrophotometer (LiCor, Lincoln, NE, model LI-6252 or LI-6262) in reference mode with a compressed gas standard of approximately 350 ppm CO<sub>2</sub> in a balance of air (Scott Specialty Gases, Longmont, CO) flowing in the reference cell. Each working standard was first calibrated against NOAA/CMDL certified CO<sub>2</sub> standards. The span and zero of the instrument are set with standards that span the atmospheric range before each analysis, and a bag of standard is analyzed at the end of each profile to check for drift in the calibration. Analysis at the ground provides highly accurate and precise measurements since all samples and standards are at the same temperature and pressure.

#### 2.4 Figures of Merit

#### 2.4.1. Precision and Accuracy

Data from the WLEF tower has shown typical summertime vertical gradients of 1-2 ppm between 51 and 496 m (Bakwin and Tans 1995). Thus, a vertical profiling technique requires very high precision; it is generally agreed that a precision and accuracy of ±0.3 ppm ( $\leq 0.1\%$ ) or better is required for deriving useful information from vertical profiles. In order to determine the inherent accuracy and precision of the bag sampling technique, a series of experiments were performed in which all twelve bags were filled with standard gas of known CO<sub>2</sub> mixing ratio and then analyzed in exactly the same manner as in the field. Tedlar<sup>TM</sup> bags were filled with 2.5 L of standard gas, and LiCor measurements were made at 1 Hz. For the flow rate of  $\approx 1$  L/min, this provided  $\approx 150$  CO<sub>2</sub> measurements per bag. The individual measurements were averaged to obtain the CO<sub>2</sub> mixing ratio for that bag. Standard deviations of measurements made for each bag were typically  $\approx 0.06$  ppm and always less than 0.1 ppm, and the standard error of the mean of the 150 measurements was always  $\leq 0.01$  ppm. However, these figures are representative of the instrumental precision only. Overall precision of the bag sampling technique can be estimated from the standard deviation of the concentrations measured for the twelve bags filled with the same standard gas. This experiment was repeated 10 times for the 396.78 ppm standard, 3 times for the 360.71 ppm standard, and 6 times for a 380.26 ppm standard. The results are summarized in Table 2.1. The average error for the three standards was 0.14 ppm or 0.037%. The average standard deviation was 0.0230 ppm or 0.061%.

#### 3.4.2 Bag Diffusion Study

The permeability of Tedlar<sup>TM</sup> bags is of concern and limits the amount of time that samples can be stored prior to analysis. Therefore, an experiment was carried out to measure the diffusion coefficient of CO<sub>2</sub> through the Tedlar<sup>TM</sup> bag membrane. Tedlar<sup>TM</sup> bags were placed in a closed container containing low concentrations of CO<sub>2</sub>. The bag was then filled with a known concentration of CO<sub>2</sub> and left for a period of time. The concentrations in the container and the bag were analyzed using the LiCor instrument. The change in concentrations in the bag and container with time were used to calculate the flux of CO<sub>2</sub> through the Tedlar<sup>TM</sup> bag membrane. Thirteen
Actual	a having an average	Standard	ness of 100 um.
CO <sub>2</sub>	Average CO <sub>2</sub>	Deviation	Difference
Ppm	ррт	(ppm)	%
396.78	396.84	0.224	0.015
	396.88	0.066	0.025
	396.91	0.109	0.033
	396.59	0.079	0.048
	396.73	0.261	0.013
	397.25	0.180	0.118
	397.70	0.231	0.232
	396.97	0.252	0.048
	396.79	0.122	0.003
(166) Rection	396.79	0.293	0.003
Average	396.94	0.182	0.054
360.71	360.89	0.249	0.050
	360.61	0.106	0.028
	360.67	0.293	0.011
Average	360.72	0.216	0.030
380.26	380.21	0.149	0.012
	380.14	0.124	0.030
	380.51	0.146	0.066
	378.87	0.215	0.366
	381.02	0.281	0.200
And Sam	380.21	0.131	0.013
Average	380.16	0.174	0.114

**Table 2.1:** Laboratory measurements of precision and accuracy of the bag samplingtechnique. Each experiment measures the mixing ratio of  $CO_2$  in 12 different bags.

conditions resulting in a well-mixed boundary layer that remained at a concern depth for the entire compling day. The concentration in the five troposphere varied by only 1-2 gum over the course of the day, as expected, while the concentration in the ABL different experiments were performed for diffusion times ranging from 2 hours to 14 hours. The average diffusion coefficient for a 3L Tedlar<sup>™</sup> bag was found to be 6.54 x 10<sup>-9</sup> cm<sup>2</sup>/s for bags having an average membrane thickness of 100 µm. This translates into a change of 0.038 ppm CO<sub>2</sub>/hr for these particular 3-L Tedlar<sup>™</sup> bags if the difference in CO<sub>2</sub> concentration between inside and outside the bag is 40 ppm, an amount at least twice as high as found between ground and elevated levels during field experiments. Diffusion would result in a significant error if the bags were not analyzed promptly after collection. Typically, our samples were analyzed within one hour of collection. Based on these measurements, and validated by experience in the field, it also important that the bags be analyzed in a room or other shelter that is well flushed with outside air, as indoor air can be up to several hundred ppm higher in concentration than sampled air.

### **2.5 Field Results**

## 2.5.1 Sample Profiles

The precision and accuracy observed in laboratory experiments carries over to field experiments as well. Given light winds, over the course of a day the concentration of  $CO_2$  within the free troposphere should be nearly constant and. Figure 2.2 shows an example of this situation. May 25, 2002 had meteorological conditions resulting in a well-mixed boundary layer that remained at a constant depth for the entire sampling day. The concentration in the free troposphere varied by only 1-2 ppm over the course of the day, as expected, while the concentration in the ABL decreased because of ecosystem exchange. This variability is likely due to advection.



Figure 2.2: Ponca City, OK 25 May 2002 CO2 Profiles

Taken 222 lines the standard deviations of measurements within the ALL, and which the first investory more from D.D.T. as D. Take. These precisions are only simplify ingles then for laboratory more series of standards, with the difference applicable to

Std. Dev. in Std. Dev. in Free Flight ABI Troposphere				
Time	ppm	ppm		
9:45	0.289	0.483		
11:00	0.127	0.520		
12:45	0.170	0.377		
14:50	0.157	0.305		
16:30	0.247	0.237		
18:30	0.530	0.341		
Average	0.253	0.377		

The proposition within the five troposphere is observed during at field missions

 Table 2.2: Standard deviations of bag samples obtained in the ABL and free

troposphere for six flights on May 25, 2002 near Ponca City, OK

compare the rest mathema, data measured at the terror. from each height over the course of a flight ware averaged to obtain a single concentration for an individual height. Figure 2.3 starows a typical comparison for a single flight. The two arethods users found to agree extremuly well

A straint accorporation and be made with the tower located near Porce City,

Table 2.2 lists the standard deviations of measurements within the ABL and within the free troposphere for each profile. The standard deviations within these wellmixed layers range from 0.077% to 0.14%. These precisions are only slightly higher than for laboratory measurements of standards, with the difference attributable to natural variability within the atmosphere.

The precision within the free troposphere is observed during all field missions. The average standard deviation of all free troposphere measurements during all six field missions was 1.015 ppm or 0.27% relative standard deviation. The average free troposphere concentration as a function of time is displayed in figure 3.22.

## 2.5.2 Comparison to Tower Measurements

Data from the bag sampler can be compared with continuous data obtained at the WLEF tower for the lower 400 m of the profiles. Tower profiles are obtained by pumping air from inlet tubes located at six fixed heights on the tower to an NDIR instrument at ground level. It takes approximately twelve minutes (two minutes of sampling at each level) to obtain a profile (Bakwin, Tans et al. 1998) In order to compare the two methods, data measured at the tower from each height over the course of a flight were averaged to obtain a single concentration for an individual height. Figure 2.3 shows a typical comparison for a single flight. The two methods were found to agree extremely well.

A similar comparison can be made with the tower located near Ponca City. Figure 2.4 compares the boundary layer CO<sub>2</sub> concentrations measured by the bag



Figure 2.3: CO<sub>2</sub> profile collected in Park Falls, WI (05/18/01) during 14:15 – 14:38 CDT. The red triangles are data from the WLEF tower, and the blue points are data obtained using the bag sampling method, with the diamonds representing bags filled on the ascent and the squares representing data from bags filled on the descent.



Time of Day CDT (min)

Figure 2.4: CO<sub>2</sub> Concentrations throughout 25 May 2002 in Ponca City, OK Measured by the Bag Sampling Method and the Ponca City AmeriFlux Tower.

alloan; therefore the gas in the reference cell was free of CO<sub>2</sub>. The measured air was

sampling method and the tower as a function of time (CO<sub>2</sub> uptake) on May 25, 2002. The absolute concentration between the two differs by an average of 1 ppm, which is acceptable considering the measurements were made at different altitudes and 20 miles apart from each other. What is of more interest is that the rate of change over the course of the day is very similar for the two methods.

#### 2.6 Measurement of Fast In-situ CO<sub>2</sub> Profiles

## 2.6.1 Motivation

Initial tests were done to determine if fast in-situ CO<sub>2</sub> measurements could be made by flying a NDIR on the PPC. The LiCor 6252 CO<sub>2</sub> analyzer can measure CO<sub>2</sub> at rates up to 10Hz, which would essentially provide a continuous profile instead of the 2 min averages provided by the bag sampling method. The motivation was to measure any small scale vertical inhomogeneity in CO<sub>2</sub> averaged out by the bag sampling method and to determine whether such averaging causes a bias in the flux calculations.

## 2.6.2 Methods

To make fast in-situ measurements, a fast response CO<sub>2</sub> analyzer was flown on the aircraft. The LiCor 6252 NDIR instrument was operated in absolute mode, meaning that the reference cell was flushed with air exiting the detection cell and passing through a CO<sub>2</sub> scrubber filled with either soda lime or ascarite (NaOH coated silica); therefore the gas in the reference cell was free of CO<sub>2</sub>. The measured air was sampled using a 12-V pump (Gast, Bridgman, MI model 3D1060-101-1081) with a flow rate of 1 L/min through a 50-cm length of 1/8-in. i.d. Teflon<sup>™</sup>-lined Tygon<sup>™</sup> tubing. The inlet tube was placed at the front of the PPC to reduce the possibility of contamination from the exhaust, but oriented to the side of the aircraft to minimize any pressure fluctuations during flight. The air was passed through a tube filled with a combination of Drierite (calcium sulfate) and magnesium perchlorate to remove water vapor and a glass fiber filter (Gelman Glass Astrodisc<sup>™</sup>) to remove particulate matter. Both the LiCor and pump were powered with a single 12-V rechargeable battery. Data were collected at 1Hz onto a data logger, which was downloaded after each flight. The LiCor was calibrated at the start of each day, using compressed CO<sub>2</sub> standard gases (Scott Specialty Gases, Longmont, CO), which had been standardized with NOAA/CMDL certified CO<sub>2</sub> standards, and the calibration was checked periodically throughout the day. The entire apparatus, except the inlet tube was placed into a Styrofoam box for protection and temperature regulation.

#### 2.6.3 Data

Initial tests were quite good. Figure 2.5(a) shows  $CO_2$  profiles measured by the continuous method and bag sampling method on May 15, 2001 in Park Falls, WI. The continuous profile has the same general shape as the bags, but with an offset, most likely caused by incorrect calibration procedure at the ground. Figure 2.5(b) shows the same profiles but with an offset of 6.1 ppm added to the continuous data. The resulting profiles matches the profile measured by the bag sampling method almost perfectly. The continuous profiles provide two important pieces of information. First, there appears to be a thin layer of lower concentration  $CO_2$  at 900 contracts where a next visible in the bag measurements. Second, the bag closest to the contracts where a second minimum and. Based on these initial results, this method for contracts were second spiller well the obtaining fast response data, provided that measure associate an events and any more thanks bag applied.



Figure 2.5: CO<sub>2</sub> profiles measured by the bag sampling method and the continuous LiCor method on (5/15/01) in Park Falls, WI. (a) is the uncorrected continuous measurement and (b) is corrected.

meters which is not visible in the bag measurements. Second, the bag closest to the surface appears to be contaminated. Based on these initial results, this method for profiling seems to work quite well for obtaining fast response data, provided that absolute measurements are made using bag samples.

Tests where the LiCor was flown on the airplane instead of the PPC did not yield as good results. Figure 2.6 shows profiles measured in Ponca City using the airplane. Although the general trend in the profiles is discernable in the descent leg, the rapid changes in pressure causes wildly varying CO<sub>2</sub> concentrations. The CO<sub>2</sub> concentration varies by as much as 5 ppm during the period of level flight when the bag samples were collected. The vertical velocity on the PPC however, is much less than the airplane and depends on the strength of rising thermals. Therefore the instrument seems unable to correct for the rapid changes in pressure and temperature experienced during flight.

Other profiles seemed to have a consistent drift of decreasing  $CO_2$  over the course of the flight (Fig. 2.7(a) and Fig. 2.8(a)); this was the most common error observed in the continuous profiles. This can be corrected using the bag samples as standards (Fig. 2.7(b) and Fig. 2.8(b)). Unfortunately, the drift is not consistent and therefore each profile must be individually corrected. This drift most likely is caused by small amounts of ambient  $CO_2$  leaking into the reference cell of the LiCor without passing through the scrubber or temperature changes during flight.

#### 2.6.4 Future Work

platform. (3/20/02) in Ponca City, OK using the arplane



Figure 2.6: CO<sub>2</sub> profiles measured on (5/20/02) in Ponca City, OK using the airplane platform.



**Figure 2.7:** CO<sub>2</sub> profiles measured using the bag sampling method and the continuous method. (a) is the uncorrected continuous data and (b) is after correcting the continuous data.

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**Figure 2.8:** CO<sub>2</sub> profiles measured by the continuous and bag sampling methods. (a) contains the uncorrected continuous data and (b) contains the corrected.

The drift observed in many of the profiles is possibly due to ambient air, containing  $CO_2$ , diffusing into the reference cell but not through the  $CO_2$  scrubber. Because it would be difficult to create a completely closed system, the best way to correct this is to put a low-flow pump inline with the reference cell and  $CO_2$  scrubber, which continually circulate the reference gas through the scrubber. This is not a unique solution, rather this is the configuration used in many continuous, stationary  $CO_2$  measurements. In the future, more rigorous pressure regulation would be needed

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## Chapter 2

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### Chapter 3: Park Falls, WI and Ponca City, OK Field Missions

# 3.1 Site descriptions and justification

Six field missions to two different locations, Park Falls, WI and Ponca City, OK, were carried out over the course of two years. The project was funded by the Great Plains Regional Center of the National Institute for Global Environmental Change (NIGEC). We collaborated with Dr. Ben B. Balsley's group from the Cooperative Institute for Research in Environmental Sciences (CIRES) and Dr. Kenneth Davis from the meteorology department at Penn State University. The goal of the study was to determine regional and seasonal variations of CO<sub>2</sub> fluxes. CO<sub>2</sub> profiles were obtained by the bag sampling method using both a small airplane and powered parachute as platforms. In addition to CO<sub>2</sub>, profiles of water vapor, temperature, and ozone also were measured.

## 3.1.1 Site selection and mission timing

The field missions were planned for the three different seasons at each site. Spring, the start of the growing season, when fluxes are dominated by the rapid draw down of CO<sub>2</sub> from photosynthesis, fall, the end of the growing season, when photosynthesis is slowing down and respiration starts to dominate and summer, the height of growing season where we expect moderate fluxes. The sites were chosen both for their different terrain and proximity to long-term CO<sub>2</sub> measurements sites. Both are rural areas in the central United States. The site near Park Falls, WI is located approximately 1.7 km from a tall tower used by NOAA/CMDL as a platform for continuous CO<sub>2</sub> profiles and fluxes and is also part of the AmeriFlux network of flux towers. This gave us an excellent opportunity to compare the bag sampling method to a well established technique. The Ponca City, OK site is dominated by short grass prairie, pasturelands, and wheat farming and is located near a 60 m tower in Lamont, OK that is a part of the AmeriFlux network of CO<sub>2</sub> flux towers. We might expect that OK, with its fast-growing plants would produce larger CO<sub>2</sub> fluxes throughout the season, whereas WI fluxes might be large in the spring, during leafout, then taper off during the summer.

## 3.1.2 Park Falls, WI

The Park Falls, WI site consists of a 3,000 m<sup>2</sup> clearing located approximately 1.6 km west of the WLEF tower, a 447-m television tower that has been used by NOAA/CMDL for continuous monitoring of the concentration and eddy covariance flux of CO<sub>2</sub> since 1994 (Bakwin, Tans et al. 1998), (Berger, Davis et al. 2001). CO<sub>2</sub> concentrations are measured by NDIR at 11, 30, 76, 122, 244, and 396 m AGL, and CO<sub>2</sub> fluxes are measured using the eddy co-variance technique at the 30, 122, and 396 m AGL. The site is located in the Chequamegon National forest approximately 10 km east of the town of Park Falls, WI (population 2,790) which is located in north central Wisconsin (45.95°N, 90.27°W, 472 m above sea level). Mixed evergreen and deciduous forest as well as boreal wetland and lowland forests dominate the region. The area has been continuously logged in since it was first settled approximately 150 years ago. This has resulted in a patchwork of old and new growth trees with some wetlands and farmland interspersed.

## 3.1.3. Ponca City, OK

The Blackwell-Tonkawa municipal airport located 30 km northeast of Ponca City, Oklahoma (population 25,919) in north central Oklahoma (36°44'43'N, 97°20"58', 310m) served as the second sampling site. The area is dominated by agriculture (predominantly wheat), grazing land and native tall-grass prairie. The site is located 20 mi SW of the Southern Great Plains ARM (Atmospheric Radiation Measurement Program) flux tower in Lamont, OK

(<u>http://public.ornl.gov/ameriflux/participants/sites</u>) (Sims and Bradford 2001). This 60m tower is also a part of the AmeriFlux program, a network of over 50 towers across North America that continuously monitor various meteorological parameters, including latent heat and  $CO_2$  flux.

#### 3.2. Sampling Platforms

As discussed below, there are a number of sampling platforms available for atmospheric measurements. Each platform has unique characteristics that make it more suitable for particular applications. We wanted a platform useful in a variety of weather conditions without severe weight restrictions and that could be used in remote areas, if necessary. We chose to use a powered parachute (PPC) as our principal sampling platform, with a Cessna 182 conventional aircraft as a backup for days when the winds are too strong for PPC flight. This study is probably the first application of the PPC to vertical profiling of chemical species in the atmosphere, and one of the ancillary goals of this work was to evaluate the PPC as a platform for such studies.

## 3.2.1 Kites and Balloons

The most common platforms for profiling the atmosphere are kites and balloons. They work very well for remote sampling, but cannot be used in populated areas because of their interference with private and commercial aircraft operations. Difficulties arise even in rural areas of the US. The US Federal Aviation Administration requires flags or lights placed every 50 ft along the tether, making it very difficult and very time consuming to raise and lower the required 3-4 km of tether. Kites and balloons also require specific weather conditions; calm winds for balloons and high winds for kites. Weight restrictions are a severe limitation with kites and balloons, and although the bag sampling method could be used with these platforms, in situ measurements with the LiCor instrument could not be made – both because of its weight and power requirements and because of the danger of losing this expensive instrument.

#### 3.2.2 Powered Parachute

For collection of air samples, the bag sampler is flown on a powered parachute (Buckeye, Falcon 582, Argos, Indiana). The powered parachute is a small, one-manned, ultralight aircraft. It consists of a single seat supported on a light aluminum frame and is powered by a 2-cycle, 65 h.p. Rotax engine fueled by regular unleaded gasoline automatically mixed with 2-cycle oil. Instead of a fixed wing, the

PPC has a parafoil parachute to provide lift. The PPC has a constant airspeed of approximately 13 m s<sup>-1</sup>, a maximum climb rate of over 5 m s<sup>-1</sup>, and a maximum decent rate of about 3 m s<sup>-1</sup>. Maximum altitude is largely determined by payload and atmospheric conditions, but typically extends to 3-4 km MSL. Takeoff and landing requires a clear and level area approximately 75 m in diameter so that the PPC can take off and land directly into the wind. The maximum payload, including the pilot, is 230 kg. The instrument package is limited more by leading-edge surface area than by weight since there must be sufficient air flow to the propeller to provide adequate thrust and reduce overall aircraft drag. As an ultralight aircraft, flights are governed by Federal Aviation Administration FAR Part 103, which limit the total weight of the aircraft itself to  $\approx 116$  kg, the fuel capacity to 20 L (approximately one hour of flight time for adequate fuel reserve during vertical profiling flights), and flights to daylight hours and VFR conditions. The PPC must be flown free of clouds; the specific rules depend on the class of airspace, but typically the aircraft must be maintained at least 150 m above, 300 m below and 600 m horizontally from clouds. No pilot license is required to operate an ultralight aircraft, but a rigorous training program is highly recommended and typically required by the manufacturer prior to sale of a PPC.

The powered parachute has many advantages as a sampling platform. Because it is a free-flight aircraft, unlike tethered kites and balloons, the PPC can operate more freely between the surface and 3-4 km, without the cumbersome necessity for tether flags or lights required by the US Federal Aviation Administration. The PPC is slower than an airplane, making it useful for vertical profiling, but not for larger-scale transect studies. Its slower speed also can be an advantage because samples can be obtained from lower altitudes more safely. Since the PPC does not require a runway for take-off or landing and is relatively lightweight, it can be transported or shipped for operations in remote regions.

The PPC does have disadvantages. The flight time is limited to 1-2 hours and it cannot be flown in high winds or through clouds. Anytime measurements are done using a manned platform there is risk of human error resulting in harm to the pilot and damage to the instruments or platform. Powered parachutes are generally considered to be very safe, due to their slow speed and built-in parachute. As with any aircraft, flight is not without risk, but danger to the pilot and aircraft can be greatly minimized through proper training, experience, and limitation of use to periods of acceptable weather conditions. The use of a PPC is not recommended without an experienced pilot.

#### 3.2.3. Airplane

When weather conditions precluded the use of the PPC, profiles were obtained using a Cessna 182 single engine aircraft. The only modification to the bag sampler was to run a 2-in diameter flexible tube from the ram air intake of the wing to the bag sampler in order to continuously flush outside air through the sampling box. Sample air was drawn through a ¼-in Teflon<sup>®</sup> tube positioned within the 2-in ram air tube. While in Wisconsin, the airplane was operated from the Park Falls airport located approximately 8 km west of the PPC site. The Oklahoma sampling site was an airport, so the airplane could be flown from the same location.

## 3.3 Other Measurements

In order to accurately determine the structure of the BL, vertical profiles of potential temperature and water vapor are needed. Temperature and relative humidity were measured with a Vaisala Humitter 50Y (Vaisala, Helsinki, Finland). Pressure was measured with a Motorola MPX415A pressure sensor (Motorola, Chicago, IL). GPS coordinates giving position, altitude; heading and ground speed were also measured along with wind speed and wind direction. Ozone mixing ratios were measured using a 2B Technologies Model 202 Ozone Monitor (2B Technologies, Golden, CO).

#### 3.4 Field Missions: Data and Results

Three field missions were performed at each site, one each during summer, winter and fall. Each mission lasted an average of ten days with the number and quality of flights depending on the weather. The flights are organized by an alpha numeric code. The first two letters depicts the site, PC for Ponca City, OK and PF for Park Falls, WI. The first number refers to the mission number and the last two to the chronological flight for the particular mission. Therefore, Flight PF306 refers to the sixth flight during the third Park Falls mission. All of the mission profiles of CO<sub>2</sub>, potential temperature, water vapor and ozone (when available) are provided in the appendices.

3.4.1 Ponca City Spring

The first Oklahoma field mission, PC1, took place during March 24, 2001 to March 31, 2001 with a total of 23 flights. It was dominated by unseasonably cold and cloudy weather. As a result, only flights during part of 3/26, 3/29 and all of 3/30 extended into the free troposphere. The average CO<sub>2</sub> mixing ratio in the free troposphere during this mission was  $375.32 \pm 1.7$ ppm. Poor weather in both Boulder and Ponca City prevented the arrival of the airplane, so all profiles were obtained with the powered parachute.

The inclement weather was accompanied by a poorly defined ABL. Figure 3.1 shows a typical set of profiles for a flight during the first Oklahoma mission. There is only a small change in the potential temperature at 800 m, the top of the ABL. The stratification in the atmosphere caused by the previous days' boundary layers is clearly visible in the water vapor profile. However, there is still a clearly defined difference in  $CO_2$  concentration in the ABL and in the free troposphere. See appendix A for all PC1 flight profiles.

Even on fair weather days, the profiles don't always indicate an ideal atmosphere. For example, Figure 3.2 shows two vertical profiles of  $CO_2$  measured on March 29, 2003. There is a clear distinction between concentrations in the ABL and free troposphere. However, there is not significant growth of the boundary layer over the time period between the two flights. Figure 3.3 depicts a better illustration of  $CO_2$ uptake throughout a day. A series of six flights were made on March 30, 2001 from 8:30 CST until 18:30 CST. The highest altitude measurements represent the concentration in the free troposphere, which are constant, as expected. Within the ABL there is a general trend of decreasing  $CO_2$  throughout the day; however, the



Figure 3.1: Ponca City, OK Flight 119 (03/30/01) 11:55 CST

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Figure 3.2: Flights PC115 and PC116 measured on March 29, 2001

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Figure 3.3: Ponca City, OK March 30, 2001 CO<sub>2</sub> Profiles

ABL concentration still remains higher than the free troposphere concentration, which is what is expected this early in spring when respiration still dominates over photosynthesis.

#### 3.4.2 Ponca City Fall

The second field mission to Ponca City, OK, PC2, took place between November 8, 2001 and November 11, 2001. This mission represented the fall and the end of the growing season. Since photosynthetic activity was beginning to shut down, a decreased amount of CO<sub>2</sub> uptake should have been observed along with a slower growth in ABL height corresponding to lower surface temperatures. Figure 3.4 is an example of data collected during the second Ponca City mission. There is a shallow boundary layer, and the CO<sub>2</sub> mixing ratio within the ABL is slightly higher than the free troposphere concentration. This is to be expected in the late fall when many of the agricultural crops have been harvested and grasslands are decaying. Figures 3.5 - 3.8 show daily CO<sub>2</sub> vertical profiles during this field mission. See appendix B for all flight data. All follow the same trend of high CO<sub>2</sub> concentrations near the ground in the early morning with a gradual decrease throughout the day without falling below free troposphere levels. The average mixing ratio in the free troposphere was  $370.48 \pm 0.78$  ppm.

#### 3.4.3 Ponca City Summer

The final field mission to Oklahoma, PF3, took place in early summer between May 19, 2002 and May 26, 2002. This represents the peak of the growing



Figure 3.4: Vertical Profiles of Potential Temperature, Water Vapor, and CO<sub>2</sub> from Flight PC216 Measured at 12:15CST on Nov. 10, 2001 in Ponca City, OK







Figure 3.6: CO<sub>2</sub> Profiles Measured on Nov. 9, 2001 in Ponca City, OK



Figure 3.7: CO<sub>2</sub> Vertical Profiles Measured on Nov. 10, 2001 in Ponca City, 2001

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season when photosynthesis dominates. Figure 3.9 shows vertical profiles where mixing ratios in the ABL are actually lower than in the free troposphere by 10:00 in the morning. This is an ideal atmospheric situation for determining  $CO_2$  fluxes by the budget method since both the ABL and free troposphere are well mixed and the height of the boundary layer is well defined. Under different synoptic conditions, different layers may exist. This is represented well in Figs. 3.10 and 3.11 where a shallow, early morning boundary layer is capped by a previous day's boundary layer. The stratification is even better illustrated in the water vapor profile (Fig. 3.12). This layer will dissipate by entraining air from the free troposphere and mixing with the ABL air as it rises.

The average concentration in the free troposphere for field experiment PF3 was  $375.91 \pm 0.58$  ppm.

## 3.4.4 Park Falls Spring

The first mission to Wisconsin, PF1, was in spring as close the start of new leaf growth as could be estimated. A total of 26 flights were made from May 15, 2001 to May 20, 2001. Weather conditions were typical for early spring, sunny and breezy, with the exception of May 15, which was too windy to fly the PPC and May 17, which was raining. The average CO<sub>2</sub> concentration in the free troposphere was  $374.6 \pm 1.2$  ppm. An example of flight data is shown in Fig. 3.13 including CO<sub>2</sub> mixing ratios measured at the WLEF tower. Figure 3.14 shows a series of profiles with the characteristic shallow, CO<sub>2</sub>-enriched ABL at 250 m which grows rapidly to 1850 m by 10:15 CDT and by 18:00 CDT has grown to 3000 m. As expected for the



Figure 3.9: CO<sub>2</sub> Profiles Measured on May 21, 2002 in Ponca City, OK


**Figure 3.10:** CO<sub>2</sub> vertical profiles measured on May 22, 2002 in Ponca City, OK showing a stratified lower troposphere.







Figure 3.12: Water vapor profile showing stratified lower atmosphere measured on May 22, 2002 at 7:31 CDT in Ponca City, OK



Figure 3.13: Flight PF209 profiles of potential temperature, water vapor and CO2 measured on May 18, 2001 at 8:36 CDT in Park Falls, WI not decrease much below the free troppephere concentration with the exception of the May 18<sup>th</sup> profiles (Fig. 3.15). By 18:50 (CDT) the concentration in the ABL is 2.6



CO<sub>2</sub> Mixing Ratio (ppm)



early spring, NPP has not reached its apex, and the  $CO_2$  mixing ratio in the ABL does not decrease much below the free troposphere concentration with the exception of the May 18<sup>th</sup> profiles (Fig. 3.15). By 18:50 (CDT) the concentration in the ABL is 2.6 ppm less than the average free troposphere concentration.

### 3.4.5 Park Falls Fall

The second field mission in Park Falls, PF2, took place in the fall from Oct. 2, 2001 to Oct 11, 2001. Most of the trees were undergoing senescence, indicating that photosynthesis had shut down and the contribution from respiration was beginning to dominate the CO<sub>2</sub> flux. The average CO<sub>2</sub> mixing ratio in the free troposphere was  $368.35 \pm 0.87$  ppm, over 6 ppm lower than in the spring. This is a result of photosynthetic activity throughout the summer. Figure 3.16 depicts typical potential temperature, water vapor and CO<sub>2</sub> profiles for a flight in the late afternoon on a warm sunny day. The well-mixed ABL has already grown to 1900m by 10:30 CST and although there is a distinct boundary break in the water vapor and potential temperature profiles, there is virtually no difference in the CO<sub>2</sub> mixing ratio between the ABL and free troposphere.

Figure 3.17 depicts a different situation in which a layer of air has most likely advected from a different region. There appear to be three distinct layers visible in the water vapor profile: a bottom layer, which contains  $5.5g/kg H_2O$ , that extends from the ground to 500m, a wetter layer (7.0 g/kg H<sub>2</sub>O) extending to 1480 m and above that is the drier, (3.5 g/kg H<sub>2</sub>O) free troposphere. These three layers are also visible in the CO<sub>2</sub> profile with the mixing ratio decreasing with each higher layer.



Figure 3.15: CO<sub>2</sub> profiles measured on May 18, 2001 in Park Falls, WI.









The middle layer persists throughout the day (Fig. 3.18), finally beginning to dissipate by 12:30 (CST) (Fig. 3.19). The mechanism for the lifetime of the middle layer can be implied by observing the changing heights and mixing ratios of H<sub>2</sub>O and CO<sub>2</sub> in each layer. The bottom layer only grows by 325 m over the course of two and a half hours by entraining air from the middle layer. This is a moderate growth rate for the early morning, indicating that the decrease in CO<sub>2</sub> concentration is more a result of photosynthesis than dilution by the air above. The boundary between the middle layer and the free troposphere changes from a sharp decrease in water vapor occurring between 1622 m and 2000 m to a gradual transition from 900 m to 2000 m. This implies a more rapid growth than that of the lower layer. The end result of this system is that this middle, wet layer is "capping" the ABL, hindering its growth.

# 3.4.6 Park Falls Summer

The final field mission in Park Falls, WI, PF3, took place from August 5, 2002 to August 13, 2002. Poor weather prevented flying during August 9-12; however the remaining days yielded an average of five flights per day, providing ample data. The average CO<sub>2</sub> concentration in the free troposphere was  $367.1 \pm 2.1$  ppm. Some interesting stratification occurred in the lower troposphere, similar to what was observed during the fall Park Falls mission (Fig. 3.20). Also, note in the CO<sub>2</sub> profile in Fig. 3.20 that the concentration in the ABL is approximately 17 ppm less than the concentration in the free troposphere. This indicates that photosynthesis is fully dominant in the summer, as was expected. This principle is illustrated in Fig. 3.21 with a series of CO<sub>2</sub> profiles measured in one day. The concentration in the free





















troposphere is constant while the concentration in the ABL is steadily decreasing throughout the day.

#### 3.5 Seasonal and Regional Trends in Free Troposphere CO2

Some general seasonal and regional trends were observed from the field missions, although with only one mission to each site in each of three seasons, it is difficult to infer long-term trends. Figure 3.22 shows the average concentration of  $CO_2$  in the troposphere for each of the three missions. The difference between spring and fall (the highest and lowest annual  $CO_2$  mixing ratios) should be greater over forests because of the larger plant mass and increased photosynthetic activity. The difference between spring and fall in Ponca City was  $4.84 \pm 1.86$  ppm, while in Park Falls it was  $6.23 \pm 1.52$  ppm

Seasonal variation in photosynthetic activity gives rise to seasonal variation in atmospheric  $CO_2$ . One would expect the atmosphere to be depleted in  $CO_2$  in the late summer and early fall because of months of photosynthesis occurring throughout the summer. In the spring, the atmosphere should contain more  $CO_2$ , resulting from winter when many plants are dormant and respiration is dominant. Finally, during the summer, increased photosynthetic activity should cause a gradual decrease in  $CO_2$ . These general trends are apparent in Fig. 3.22 except for the summer concentration in Ponca City, which is 5.4 ppm higher than the November concentration. This is not too unexpected for that early in the summer; however the summer  $CO_2$  is also slightly larger than the previous spring's concentration. The IPCC estimates a net global annual  $CO_2$  increase of 1.5 ppm/yr (IPCC 2001), and perhaps that explains part of the







Figure 3.22: Average CO<sub>2</sub> concentration during each field mission. The March-01 Ponca City and May01 Park Falls points represent spring missions, the October and November points represent fall missions, and the August-02 Park Falls and May-2 Ponca City represent summer missions. The Niwot Ridge points are monthly averages measured at the NOAA/CMDL Niwot Ridge tower. discrepancy. This, however, was not observed in the Park Falls data, implying that the northern forests are a larger net sink for  $CO_2$  than the mid-latitude grasslands, which is what we expected.

Figure 3.22 also contains monthly average CO<sub>2</sub> mixing ratios during 2001 measured at Niwot Ridge, CO (40°3'N, 105°35'W). The Niwot Ridge tower is part of the NOAA/CMDL Carbon Cycle Greenhouse Gases Group cooperative air sampling network (<u>http://www.cmdl.noaa.gov/</u>) and at an altitude of 3475 meters, it is a good approximation of free tropospheric air. Both the trends and mixing ratios measured at the three different sites are fairly consistent for the spring and fall missions, it is difficult to compare the summer data, as 2002 data at Niwot Ridge is not available. The difference between the Niwot Ridge and Park Falls data during the summer was 1.32 ppm and 0.96 ppm during the fall. The difference between CO<sub>2</sub> mixing ratio measured at Niwot Ridge and Ponca City was 1.00 ppm and 0.61 ppm in the fall. The fact that our measurements differ by less than 1.5 ppm indicates that we are successfully measuring CO<sub>2</sub> mixing ratios in the free troposphere.

# Chapter 3

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# Chapter 4: Carbon Dioxide Flux Calculations

#### 4.1 Introduction and Motivation

A flux is a measurement of the rate of change of a scalar or energy integrated over time and space. Temporal variations of average mixing ratios of CO<sub>2</sub> provide some insight into causes of CO<sub>2</sub> changes on annual to decadal scale. However, measurements of fluxes provide more detailed mechanistic information on specific source/sink strengths. Fluxes provide various spatial resolutions, depending on the method used. Techniques span the range of photosynthesis and respiration rates for a single plant species to storage capacity of an entire region. Flux information at all scales is important not only in understanding climate and biological processes, but also for verifying and improving climate models (Baldocchi, Falge et al. 2001).

### 4.1.1 Important concepts in boundary-layer meteorology

The atmospheric, or convective boundary layer is defined as the lowermost layer of the atmosphere that is directly influenced by the Earth's surface and responds to surface forcing on timescales of an hour or less (Stull 1988). The height of the ABL can vary from tens of meters if the air is stably stratified, which generally occurs at night when the air closest to the surface is colder than the air above it, to a few kilometers, usually occurring during a sunny day when the air close to the surface rises convectively (Dabberdt, Lenschow et al. 1993).

The boundary layer is often made up of other layers: the surface layer, mixed layer (ML), and stable or, nocturnal, layer (NBL). When clouds are present, the mixed layer is further subdivided into a cloud layer and sub-cloud layer. The surface

layer, which is the lowest portion of the ABL, is greatly influenced by the surface, and turbulent mixing is caused primarily by wind shear (Dabberdt, Lenschow et al. 1993). Mixing in the mixed layer is convectively driven by both radiative cooling from a cloud layer and heat transfer from the ground surface (Stull 1988). On a cloudless day, growth of the ML is dominated by buoyant plumes. Shortly after sunrise, the ML begins to grow in depth. This growth is caused by rising thermals from the ground, which also causes intense vertical mixing. The ML reaches its maximum depth in the mid-afternoon. The growth is facilitated by entrainment of cool, stable air from the free troposphere. The layer above the ML is quite stable, creating a lid on the ABL. The area between the top of the ABL and bottom of the free troposphere is called the entrainment zone because it is composed of air that is entrained into the ABL as it grows. This stable layer can also act as a lid to pollutants, since most pollution sources are close to the ground; however scalars can be transported into the FT by large eddies.

Growth of the ABL over the course of a day is not always spatially uniform. Both surface heterogeneity and clouds can create a patchwork affect in the ABL, with different areas conducting heat to the surface layer to varying degrees. As a result, adjoining parcels of land can generate air parcels with different vertical velocities and create large eddies, which are difficult to predict and correct for, making them a significant ( $\pm 10\%$ ) source of error for micrometeorological methods of measuring fluxes (Baldocchi 1997).

#### 4.2 Methods for determining CO<sub>2</sub> Fluxes

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### 4.2.1 Enclosure Methods

Enclosure or chamber methods involve enclosing a parcel of ground, vegetation or water with either a rigid chamber or bag. The flux is then directly measured as the rate of change in concentration. Chamber methods are simple, inexpensive and portable, making them attractive methods for many applications. There are a number of variations on this concept such as a closed dynamic chamber in which the concentration in the chamber is incrementally increased from 20ppm below ambient levels to 20ppm above ambient and the concentration measured with an external NDIR, and a closed static chamber in which samples from within the chamber are periodically obtained with a syringe and analyzed externally (Norman, Kucharik et al. 1997). Also popular are open flow chamber methods which flow a continuous stream of air through the chamber, and the concentration at the inlet and outlet are both analyzed (Guenther, Zimmerman et al. 1996). The closed dynamic method is considered to be the most accurate because it minimizes errors due to leaks into or out of the system. The open flow method has the advantage of providing continuous long-term, unattended measurements.

In general, enclosure methods are best used to determine fluxes for individual plants leaves or ground surfaces, and they provide crucial information on specific trace gas sources and mechanisms for ecosystem exchange. It is possible to extrapolate enclosure fluxes to a region; however, detailed information of the ecosystem structure is necessary, and the placement of the enclosures must be representative of the area. Large uncertainties are common due to disturbances arising from the chambers themselves (Dabberdt, Lenschow et al. 1993). Deviations of temperature, pressure,  $CO_2$ , water vapor and solar radiation as a result of changes in atmospheric conditions all can affect the flux. Even well regulated systems can yield uncertainties of ±10% (Guenther, Zimmerman et al. 1996) to ±100% (Dabberdt, Lenschow et al. 1993).

Waring, Law at al. 1995). The method implies that CO<sub>2</sub> and series yelocity an

#### 4.2.2 Eddy Covariance

Eddy covariance is a micrometeorological technique where the flux is "the average of the instantaneous product of vertical velocity (w) and constituent density or mixing ratio with respect to air" (Dabberdt, Lenschow et al. 1993). If c is the mixing ratio of a scalar with respect to dry air, than the flux is given as:

$$F_c = (\overline{c'w'})$$

where w is the vertical velocity, prime designates the deviation from the mean and the overbar signifies a time average (Verma 1990). These fluxes are valid under steady state conditions and horizontally homogeneous conditions. Deviations from steady state conditions are discussed below.

Instrumentation for eddy covariance flux measurements includes an accurate CO<sub>2</sub> sensor with a fast response time. NDIR is the commonly used (Verma 1990), (Haszpra, Barcza et al. 2001), (Baldocchi, Valentini et al. 1996), (Bakwin and Tans 1995). To measure the wind speed and direction, a sonic anemometer is used which works by measuring the time required for a sound wave to travel between two points.

(1)

Sampling rates range from 4Hz (Haszpra, Barcza et al. 2001) to 20Hz (Baldocchi, Falge et al. 2001) in order to ensure sampling of high frequency elements of the flux. Measurements are than averaged over a time which is larger than the period of turbulent motion. Instruments are generally mounted on towers or flown on aircraft (Waring, Law et al. 1995). The method implies that  $CO_2$  and vertical velocity are measured at the same time and place, which is not a trivial matter. Tower instrumentation is usually configured in one of two ways; either with a closed-path CO<sub>2</sub> sensor at the ground with sampling tubes located in or near the anemometer or with an open-path system located at the anemometer. There are advantages and disadvantages to each method (Leuning and Judd 1996). The primary advantage to an open-path sensor is that it eliminates errors due to long sampling tubes and therefore makes flux calculations simpler. However, open-path systems require more operator attention to calibrate and are exposed to all environmental conditions, making them more susceptible to drift caused by diurnal temperature changes. Consideration must also be made to site selection. An ideal site is on a flat portion of land with uniform and representative vegetation (Baldocchi, Falge et al. 2001). Another consideration is the placement of the instruments in relation to the tower. Aerodynamic flow distortions can cause deviations of  $\pm 50\%$  of real wind speeds (Haszpra, Barcza et al. 2001).

Eddy covariance is a useful method for measuring fluxes. Unlike enclosure methods, it causes minimal disturbances to the microenvironment of the ecosystem being measured. Continuous, long-term measurements over the course of many months may be made without any operator attention. It also provides fluxes that are integrated over much larger spatial regions than chambers. Although there are no simple ways to determine the flux footprint of a tower, qualitatively, the flux foot print increases with increasing measurement height; however differences and homogeneity in regional ecology, weather conditions and tower environment all contribute (Baldocchi 1997). Flux footprints for towers are of the order of square kilometers, and fluxes measured by aircraft methods can be around 100 km<sup>2</sup>. Aircraft measurements of fluxes are of particular use, as this is similar to the grid size of global models (Ruimy, Kergoat et al. 1996).

Even with rigorous attention to correction for possible error, random errors arise from inhomogeneous terrain and instable atmospheric conditions for towerbased fluxes, which are difficult to predict or correct for. (Baldocchi, Valentini et al. 1996) suggest that even intermittent passage of large eddies can cause temporal sampling error to be at least  $\pm 10\%$  on an hourly time scale. For this reason, occasional aircraft measurements are suggested to compliment and verify towerbased measurements as well as to extend tower data to a landscape scale (Baldocchi, Valentini et al. 1996), (Dabberdt, Lenschow et al. 1993), (Verma 1990).

### 4.2.3 BL Budget Method

Regional scale  $CO_2$  fluxes can be calculated from vertical profiling data using the boundary layer budget method (Munley Jr. 1991), (Kuck 1999), (Denmead, Raupach et al. 1996). To calculate fluxes by this method one must monitor the  $CO_2$ mixing ratio within the ABL, the height of the ABL and the  $CO_2$  concentration being entrained from above, all as a function of time. This is accomplished by making multiple vertical profiles through the day. We must also assume that the boundary layer is well mixed and shallow compared to the free troposphere. The governing equation for the change in  $CO_2$  in a column of air from z = 0 to z = h in time t is

$$\left(\frac{dCO_{2,BL}}{dt}\right) = \frac{F_c}{h} + \left(\frac{CO_{2,EZ} + CO_{2,BL}}{h}\right) \left(\frac{dh}{dt} - W_{+}\right)$$
(2)

Where  $F_c$  is the flux density at the ground, *h* is the height of the ABL,  $CO_{2,EZ}$  is the concentration of CO<sub>2</sub> in the entrainment zone,  $CO_{2,BL}$  is the concentration in the ABL and  $W_+$  is the average vertical velocity at the top of the ABL.  $W_+$  is typically very small compared with the change in the height of the boundary layer, in which case equation (1) can be rearranged to yield:

$$F_{c} = h \left( \frac{dCO_{2,BL}}{dt} \right) - \left( CO_{2,EZ} - CO_{2,BL} \right) \left( \frac{dh}{dt} \right)$$
(3)

This allows surface fluxes to be calculated from measurements of h,  $CO_{2,FZ}$ , and  $CO_{2,BL}$ .

### 4.3 Flux Calculations

### 4.3.1 Determination of the height of the ABL

In order to calculate fluxes via the BL budget method, a way of determining the height of the ABL must be identified. The most common ways to do this are by observing potential temperature,  $\theta$ , and water vapor vertical profiles. Potential temperature is defined as the temperature that dry air must have to equal the density of moist air at that pressure (Stull 1988). It's really a measure of the buoyancy or density of an air parcel. Incoming solar radiation heats up the surface of the earth, and some of this heat transfers to the air that is in direct contact with the ground; this air is, by definition, the ABL. The air becomes hot (more buoyant) and rises, mixing in air from above. Air in the free troposphere is not in contact with the ground and does not absorb much of the incoming solar radiation and therefore is less buoyant than air in the ABL. A measure of the buoyancy of air, such as  $\theta$ , as a function of altitude shows the boundary between the ABL and the free troposphere as a sharp decrease in potential temperature.

Water vapor profiles can also be used to determine the depth of the ABL. Because the entrainment zone is quite stable it acts like a lid on the ABL. Therefore the mixing ratio of anything with a source at the surface will tend to have a constant mixing ratio in the ABL, but will decrease rapidly at the free troposphere; the sudden change in mixing ratio identifies the boundary between the two layers. Most water vapor originates at the surface, caused by evaporation from lakes, ponds or other bodies of water, is present in large amounts throughout the world, and is simple to measure. This makes it ideal for determination of the ABL; however, any pollutant with a source at the surface can also serve this purpose. Figure 4.1 shows potential temperature and water vapor profiles measured in Park Falls. The boundary between the ABL and free troposphere is clearly evident at 1700 m by the sharp increase in





manual temperature and decrease to water vapor mixing ratio. Figure 4.2 shows at manuals of the prowth of the A SL cover the course of a day.





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potential temperature and decrease in water vapor mixing ratio. Figure 4.2 shows an example of the growth of the ABL over the course of a day.

# 4.3.2 CO<sub>2</sub> Fluxes in Ponca City, OK

CO<sub>2</sub> fluxes were calculated for two days in the spring, March 26<sup>th</sup> and 30<sup>th</sup>, one day in the fall, November 10<sup>th</sup> and one day in the summer, May 25<sup>th</sup>. Surface fluxes, averaged over the length of a flight, approximately one hour, measured throughout the day in Ponca City are shown in Fig. 4.3. Negative fluxes indicate CO<sub>2</sub> being drawn down to the surface. The downward fluxes all have a trend of increasing throughout the day, with the exception of the springtime measurements. This is expected as photosynthetic activity generally increases during the day. Seasonal trends are also evident in the data. The daily average CO<sub>2</sub> fluxes on March 26<sup>th</sup> and 30<sup>th</sup> are  $-0.12 \pm 0.07$  ppm m/s and  $-0.13 \pm 0.11$  ppm m/s, which are similar to the early summer flux ( $-0.17 \pm 0.08$  ppm m/s and larger in absolute magnitude than the average daily flux measured in the fall,  $-0.03 \pm 0.09$  ppm m/s. We would expect the flux in the late fall to be very close to zero, or even positive because of decreased plant growth.

# 4.3.3 CO<sub>2</sub> Fluxes in Park Falls, WI

CO<sub>2</sub> fluxes were calculated for five days in Park Falls, October 7<sup>th</sup> and 9<sup>th</sup>, May 18<sup>th</sup>, and August 6<sup>th</sup> and 8<sup>th</sup>. Figure 4.4 shows the hourly averaged fluxes for the Park Falls field missions. Fluxes vary by 1 ppm m/s, which is much greater than was observed during the Ponca City missions. The daily averaged downward fluxes for



Figure 4.3: Hourly averaged surface fluxes measured in Ponca City, OK. (CST = UTC - 6, CDT = UTC - 5)



Figure 4.4: Surface fluxes measured in Park Falls, WI

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the summer months (August 6 and 8) were much larger ( $-0.33 \pm 0.3$  ppm m/s and  $-0.43 \pm 0.24$  ppm\*m/s) than observed in the early summer in Ponca City. This is indicative of increased photosynthetic activity. Similar seasonal differences were observed in Park Falls; the daily averaged flux on May 18 was  $-0.19 \pm 0.25$  ppm\*m/s, which was larger than the late summer flux and smaller then the observed fall fluxes  $(0.14 \pm 0.3 \text{ ppm*m/s on } 10/7 \text{ and } -0.02 \pm 0.07 \text{ ppm*m/s on } 10/9).$ 

#### 4.3.4 Comparison to Tower Data

Average daily surface fluxes measured using profiles collected by the bag sampling method and calculated via the ABL budget method were compared to the surface fluxes measured at the near-by flux towers using the eddy covariance method (Hurwitz, Davis et al. 2003) (Fig. 4.5). Fluxes were measured at the WLEF tower in Park Falls, WI at 30, 122, and 396 meters (Berger, Davis et al. 2001) and at 60 meters at the ARM tower in Lamont, OK (Sims and Bradford 2001). As indicated in Fig. 4.5, the agreement is quite good for certain days, in particular 10/7/2001, 10/9/2001, 3/26/2001, and 5/18/2001. The r.m.s. difference between fluxes measured at the tower and from aircraft is generally less than 0.3 ppm m/s (Hurwitz, Davis et al. 2003).

#### 4.4 Advection

It has been suggested that the differences between tower and aircraft flux measurements can be reconciled by taking into account the role of horizontal advection (Hurwitz, Davis et al. 2003). Advection or horizontal gradients of CO<sub>2</sub>, is the second second



Figure 4.5: Comparison of tower and aircraft surface fluxes (Hurwitz, Davis et al. 2003).

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caused by surface heterogeneity and is usually considered to be negligible in eddy covariance measurements (Baldocchi, Finnigan et al. 2000). In fact, the advection term, integrated over typical tower height (40-200m) is probably very small, particularly as compared to the turbulent flux term. However, for aircraft measurements, which integrate over the entire height of the ABL, neglecting horizontal advection could result in a significant error.

Assuming that the differences in the boundary layer budget fluxes and tower fluxes are due to advection, horizontal advection can be determined from the difference in net ecosystem exchange (NEE) between the aircraft and tower. NEE is determined for both methods by applying a budget equation for scalar quantities, in this case  $CO_2$  (Yi, Davis et al. 2001) and making the following assumptions: in a well-mixed ABL, the vertical advection term is much smaller than the horizontal advection term and is therefore ignored, and since the chemical reactions which produce  $CO_2$  at the surface are assumed to be very slow, the source of  $CO_2$  at the ground is assumed to be zero. Taking these assumptions into account and integrating over the measurement height yields the following equation (Yi, Davis et al. 2001):

$$\int_{0}^{2r} \frac{\partial \bar{c}}{\partial t} dt + \int_{0}^{2r} \bar{u} \frac{\partial \bar{c}}{\partial x} dt + (\overline{w'c'})_{Zr} = (\overline{w'c'})_{0} = NEE$$
(4)

The overbar represents an hourly mean and the prime designates a deviation from the mean. The equation is the sum of the surface flux, horizontal advection and the turbulent flux, all of which, except the surface flux and horizontally integrated
advection term are provided by tower data. NEE for the aircraft data is described as the sum of the surface flux, which is determined by the boundary layer budget method and the entrainment flux, which can be calculated by the following equation (Hurwitz, Davis et al. 2003):

$$Fz_{i} = \left(\frac{\partial z_{i}}{\partial t} + \overline{w}\right) \Delta_{z} CO_{2}$$
(5)

where  $\Delta_z CO_2$  is the difference in  $CO_2$  mixing ratio between the entrainment zone and the ABL. The equation can be further simplified by assuming that the vertical velocity (w) at the top of the ABL is very small compared with the growth of the ABL. Therefore, the entrainment flux is only dependent on the jump in  $CO_2$  at the top of the ABL and the growth of the ABL. Advection is then inferred via the following equation (Hurwitz, Davis et al. 2003):

$$\begin{pmatrix} z_{i} \\ 0 \\ \overline{\partial t} \\ \partial t \\ dz + \frac{\partial z_{i}}{\partial t} \Delta_{z} CO_{2} \end{pmatrix} - \begin{pmatrix} z_{r} \\ 0 \\ \overline{\partial t} \\ \partial t \\ dz + \int_{0}^{z_{r}} \overline{u} \frac{\partial \overline{c}}{\partial x} dz + (\overline{w'c'})_{Zr} \end{pmatrix} = NEE_{aircraft} - NEE_{tower} = \begin{pmatrix} z_{r} \\ 0 \\ \overline{\partial t} \\ \partial x \\ \partial x \\ dz - \int_{0}^{z_{i}} \overline{u} \\ \overline{\partial x} \\ \partial x \\ dz \end{pmatrix}$$
(6)

Advection, calculated via equation 6, using data obtained on seven different days in Park Falls and Ponca City and data from the WLEF tower and ARM tower are shown in Fig. 4.6. Daily average advection terms were generally less than I ppender, however, hearty advances approached 3 opender (Harwitz, Davis et al. 2003). These results imply homenessi Ciby gastients of 0.0) to 4 ppendicks (Harwitz, Davis et al. 2003). These values may not be representative due to the PPC's inshiftey to collect data en standy or gasty days. Also, one must assume that the time averaged over both tower and asternit sorther frame was the same how the



Figure 4.6: Advection of CO<sub>2</sub> calculated on seven different days in Park Falls, WI and Ponca City, OK (Hurwitz, Davis et al. 2003).

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1 ppm/hr; however, hourly advection approached 3 ppm/hr (Hurwitz, Davis et al. 2003). These results imply horizontal  $CO_2$  gradients of 0.01 to 4 ppm/10km (Hurwitz, Davis et al. 2003). These values may not be representative due to the PPC's inability to collect data on windy or gusty days. Also, one must assume that the time averaged over both tower and aircraft surface fluxes was the same as was the regional area.

Further investigation of the role of advection in fair weather situations could be very useful in correlating tower and aircraft fluxes as well as determining horizontal gradients and the role of surface heterogeneity in flux uncertainties. Horizontal gradients could be measured by flying transects over the flux footprint and using those data to correct aircraft-derived surface fluxes. To test this theory, CO2 was measured on a horizontal transect flight during the spring Ponca City field mission on May 21, 2002. The Cessna was flown into the direction of the wind for approximately 380km, than returned on the same flight track. The CO<sub>2</sub> was measured by both bag samples and continuous LiCor. Figure 4.7 shows the CO<sub>2</sub> mixing ratio verses flight traveled. A clear gradient is evident with all data agreeing well with each other. The measured horizontal gradient of CO<sub>2</sub> was an average of 0.260 ppm/10km. This is within the range hypothesized by the above study meaning that horizontal advection could very well play a role in the differences between fluxes measured via the tower-based eddy covariance and the budget method. Unfortunately time prevented us from making additional transect flights to further test this theory.



Figure 4.7: CO<sub>2</sub> mixing ratio measured in Ponca City, OK on May 21, 2002 by bag sampling method and continuous LiCor method during level flight at 600m altitude to determine horizontal CO<sub>2</sub> gradient.

# Chapter 4

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### **Chapter 5: Summary**

### **5.1 Conclusions**

The global carbon cycle is still not well understood, the main uncertainty being the magnitude of the terrestrial  $CO_2$  sink in the Northern Hemisphere. This is largely due to the lack of monitoring sites on land. Carbon dioxide fluxes measured on a few towers by eddy covariance are expected to be reasonably accurate, but each site characterizes only a small footprint. Furthermore, it is highly desirable to greatly increase the number of  $CO_2$  measurements made in the free troposphere as input to inverse modeling studies that are free of the complications of boundary layer meteorology. For these reasons, an inexpensive, portable and accurate method for measuring vertical profiles of  $CO_2$  is necessary in order to better understand the global carbon biogeochemical cycle.

## 5.1.1 Bag Sampling Method

The vertical profiling technique reported here exhibits precision and accuracy of 0.023 and 0.14 ppm<sub>v</sub>, respectively, which is more than adequate for studies of atmospheric variability of CO<sub>2</sub>, including measurements of landscape-scale fluxes and the concentration gradient across the top of the ABL. CO<sub>2</sub> mixing ratios measured by the bag sampling method generally differed from those measured on nearby flux towers by less than 0.5%. The Tedlar<sup>™</sup> bag sampling method has been used on both small plane and PPC platforms successfully and could be modified for balloons and kites, making it a good method for profiling in remote areas. Bag sampling has the advantage over flask sampling in that it averages over small eddies yet still providing detailed information on the variability of  $CO_2$  concentrations through the ABL. In particular, we are clearly able to quantify the "jump" in concentration at the top of the boundary layer over the course of the day, something which is not observable by towers as they are not tall enough to sample in the free troposphere.

The only major disadvantage to the bag sampling method is that it is quite user intensive and therefore cannot provide long term or continuous measurements nor are measurements easily obtained by untrained personal.

#### 5.1.2 Field Missions

The bag sampling method was used successfully in six field missions, three in Park Falls, WI and three in Ponca City OK, resulting in more than 150 vertical profiles. In addition to CO<sub>2</sub> profiles, very precise H<sub>2</sub>O profiles were also obtained. The 1Hz measurements of relative humidity translate into an approximate altitude resolution of a measurement every 2 to 4 meters. This represents some of the best, most comprehensive water vapor profiles available. These provide valuable information on the structure of the lower troposphere and could be helpful in obtaining and understanding latent heat fluxes.

We were able to observe the daily drawdown of  $CO_2$  and the corresponding boundary layer growth. The daily and seasonal trends in  $CO_2$  mixing ratio and profiles we observed were consistent with what was expected based on our knowledge of the global carbon cycle and boundary-layer meteorology. The observed boundary layer growth reached 2400m on spring and summer days but only a modest 1800m during fall campaigns.

One of the most important products of these field missions was the record of  $CO_2$  concentrations in the free troposphere. These types of measurements are more costly and difficult to obtain and are therefore relatively scarce. Flux towers generally estimate free troposphere concentrations or obtain them from the rare airplane campaigns which make measurements over a wide swath of the country a few days out of the year. Our measurements show that although CO<sub>2</sub> mixing ratios changed little in comparison to those in the boundary layer, there are observable seasonal and regional trends. These trends are caused by the periodic deep convective mixing of boundary layer air into the free troposphere during the passage of large weather events. CO<sub>2</sub> mixing ratios in Park Falls are on average 1 to 2 ppm lower than those in Ponca City due to forested regions larger capacity for CO<sub>2</sub> uptake which leaves the boundary layer in the northern forest depleted in CO<sub>2</sub> as compared with the grasslands in OK. Similar trends on an inter-annual scale are also observed with late summer tropospheric air depleted in CO<sub>2</sub> from the summer's extensive photosynthetic uptake depleting the boundary layer which in turn mixes into the free troposphere. We observed an average inter-annual variation of 5.5 ppm. Although this is a seemingly insignificant variance compared with the diurnal trend in ABL  $CO_2$ , it is still important to fully quantitate.

## 5.1.3 Flux and Advection

Using the data collected during the field missions, fluxes were calculated using a boundary-layer budget method. Both seasonal and regional variations were observable and were consistent with what was expected. The largest negative (downward) fluxes were observed during the summer missions and the smallest negative fluxes observed during the fall. The greatest seasonal variation was observed in Park Falls, the forested site, with a difference of 0.44 ppm m/s between summer and fall fluxes compared to a summer to fall difference of 0.14 ppm m/s in Ponca City. The fluxes we calculated agree fairly well with those measured on nearby flux towers via eddy covariance, particularly under fair weather conditions.

Differences in tower and aircraft flux measurements may be partially due to differences in the sizes of the footprints sampled by the two techniques ( $\approx 1 \text{ km}^2$  for towers vs. 100 km<sup>2</sup> for aircraft measurements). However, horizontal advection also will lead to a discrepancy in fluxes measured by the two techniques. If the latter is true, advection can be defined as the difference between net ecosystem exchange (NEE) measured by aircraft and tower. Horizontal advection at Ponca City and Park Falls ranged from -0.0004 ppm/s to 0.0001 ppm/s, implying horizontal CO<sub>2</sub> gradients of 0.01 to 4 ppm/10km. During our initial study on this theory, we measured a horizontal gradient of CO<sub>2</sub> of 0.260 ppm/10km. This is precisely what was implied from the average difference in fluxes between the eddy covariance and boundary-layer budget methods, leading us to believe that horizontal advection may be an important piece of the flux puzzle.

#### **5.2 Future Work**

There is much more work to be done in this area of research. First, in order to ascertain a better understanding of seasonal and regional variations and trends, many more missions to Park Falls and Ponca City are required. From this, any biases that may occur in current tower methods can be identified, investigated, quantified and eventually corrected for making subsequent towers more representative of true regional scale surface fluxes.

Our current understanding of the global carbon cycle is primarily limited by the lack of data over land. Small-scale, plant level, carbon processes are fairly well understood but the correlation of these events with atmospheric and meteorological processes requires further study. Therefore, more data collected at sites which are not currently being investigated via tower-based flux methods are also needed to obtain a clear picture of CO<sub>2</sub> concentrations and surface fluxes over terrestrial site throughout the United States.

From an instrumental point of view, more work needs to be done on the insitu  $CO_2$  profiling method discussed in chapter two to either find a correction for the temperature dependence or develop a method to better control the temperature of the instrument and sample gas stream. Continuous profiles will provide more detailed information of the structure and perhaps transport of atmospheric  $CO_2$  over terrestrial ecosystems.

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Appendix A: Ponca City Spring Profiles

Ponca City, OK Flight 101 (03/25/01) 19:00 CST



Ponca City, OK Flight 102 (03/25/01) 9:45 CST







Ponca City, OK Flight 104 (03/25/01) 12:00 CDT







Ponca City, OK Flight 106 (03/25/01) 16:15 CST











Ponca City 1 Flight 109: (03/26/01) 14:15 CST



Ponca City, OK Flight 110 (03/26/01) 15:36 CST



Ponca City, OK Flight 111 (03/26/01) 17:00 CST



Ponca City, OK Flight 115 (03/29/01) 16:50 CST



Ponca City, OK Flight 116 (03/29/01) 17:50 CST



Ponca City, OK Flight 117 (03/30/01) 8:30 CST



Ponca City, OK Flight 118 (03/30/01) 10:10 CST







Ponca City, OK Flight 121 (03/30/01) 15:30 CST



Ponca City, OK Flight 122 (03/30/01) 17:01 CST




Ponca City, OK Plane Flight 202 (11/08/01) 11:00 CST



Ponca City, OK Plane Flight 203 (11/08/01) 12:30 CST











Ponca City, OK PPC Flight 208 (11/09/01) 13:45 CST



Ponca City, OK Plane Flight 209 (11/09/01) 16:15 CST



Ponca City, OK Plane Flight 210 (11/09/01) 19:25 CST







Ponca City, OK Plane Flight 212 (11/10/01) 6:20 CST



Ponca City, OK PPC Flight 213 (11/10/01) 8:30 CST



Ponca City, OK PPC Flight 214 (11/10/01) 9:40 CST



Ponca City, OK PPC Flight 215 (11/10/01) 10:55 CST







Ponca City, OK PPC Flight 217 (11/10/01) 13:45 CST











Ponca City, OK Plane Flight 220 (11/11/01) 16:00 CST



Ponca City, OK Plane Flight 301 (05/19/02) 11:09 CST



Ponca City, OK Plane Flight 302 (05/19/02) 13:08 CST



Ponca City, OK Plane Flight 306 (05/21/02) 10:17 CST



Ponca City, OK Plane Flight 308 (05/21/02) 14:50 CST









Ponca City, OK Plane Flight 311 (05/22/02) 9:18 CST



Ponca City, OK Plane Flight 313 (05/25/02) 9:37 CST



Ponca City, OK Plane Flight 315 (05/25/02) 12:40 CST



Ponca City, OK Plane Flight 316 (05/25/02) 14:45 CST







Ponca City, OK Plane Flight 318 (05/25/02) 18:00 CST







Ponca City, OK Plane Flight 320 (05/26/02) 9:14 CST



Ponca City, OK Plane Flight 321 (05/26/02) 11:00 CST





Park Falls, WI PPC Flight 203 (05/16/01) 12:20 CDT






Park Falls, WI PPC Flight 205 (05/16/01) 15:30 CDT







Park Falls, WI PPC Flight 207 (05/17/01) 10:10 CDT



Park Falls, WI PPC Flight 209 (05/18/01) 8:36 CDT



Park Falls, WI PPC Flight 210 (05/18/01) 10:06 CDT



Park Falls, WI PPC Flight 211 (05/18/01) 11:40 CDT



Park Falls, WI PPC Flight 212 (05/18/01) 13:00 CDT



Park Falls, WI PPC Flight 213 (05/18/01) 14:15 CDT



Park Falls, WI PPC Flight 214 (05/18/01) 15:30 CDT



Park Falls, WI PPC Flight 215 (05/18/01) 16:50 CDT



Park Falls, WI PPC Flight 216 (05/18/01) 18:00 CDT



Park Falls, WI PPC Flight 217 (05/19/01) 8:52 CDT







Park Falls, WI PPC Flight 219 (05/19/01) 11:30 CDT



























Park Falls, WI Plane Flight 226 (05/20/01) 15:50 CDT











Park Falls, WI PPC Flight 304 (10/2/01) 8:30 CST



CO<sub>2</sub>

Water Vapor

Potential Temperature

3000

3000 1

Park Falls, WI PPC Flight 305 (10/4/01) 9:45 CST























Park Falls, WI Plane Flight 313 (10/6/01) 9:30 CST















Park Falls, WI PPC Flight 317 (10/7/01) 11:36 CST










Park Falls, WI PPC Flight 320 (10/7/01) 15:15 CST



Park Falls, WI PPC Flight 321 (10/7/01) 16:30 CST



Park Falls, WI PPC Flight 323 (10/9/01) 9:00 CST



















Park Falls, WI PPC Flight 328 (10/9/01) 14:45 CST



Park Falls, WI PPC Flight 329 (10/11/01) 10:15 CST



Park Falls, WI PPC Flight 330 (10/11/01) 11:30 CST



## Park Falls, WI PPC Flight 401 (8/5/02) 11:37 CDT





Park Falls, WI PPC Flight 404 (8/5/02) 16:52 CDT































Park Falls, WI PPC Flight 412 (8/7/02) 8:01 CDT







Park Falls, WI PPC Flight 414 (8/7/02) 11:10 CDT



















Park Falls, WI PPC Flight 419 (8/8/02) 9:35 CDT















Park Falls, WI PPC Flight 424 (8/8/02) 17:19 CDT



Park Falls, WI PPC Flight 423 (8/8/02) 15:48 CDT







Park Falls, WI PPC Flight 426 (8/13/02) 1:17 CDT




Park Falls, WI PPC Flight 428 (8/13/02) 16:22 CDT

