Seasonally varying contributions to urban CO$_2$ in the Chicago, Illinois, USA region: Insights from a high-resolution CO$_2$ concentration and $\delta^{13}$C record

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Abstract

Understanding urban carbon cycling is essential given that cities sustain 54% of the global population and contribute 70% of anthropogenic CO$_2$ emissions. When combined with CO$_2$ concentration measurements ([CO$_2$]), stable carbon isotope analyses ($\delta^{13}$C) can differentiate sources of CO$_2$, including ecosystem respiration and combustion of fossil fuels, such as petroleum and natural gas. In this study, we used a wavelength scanned-cavity ringdown spectrometer to collect $\sim 2 \times 10^6$ paired measurements for [CO$_2$] and $\delta^{13}$C values in Evanston, IL for August 2011 through February 2012. Evanston is located immediately north of Chicago, IL, the third largest city in the United States. The measurements represent one of the longest records of urban [CO$_2$] and $\delta^{13}$C values thus far reported. We also compiled local meteorological information, as well as complementary [CO$_2$] and $\delta^{13}$C data for background sites in Park Falls, WI and Mauna Loa, HI. We use the dataset to examine how ecosystem processes, fossil fuel usage, wind speed, and wind direction control local atmospheric [CO$_2$] and $\delta^{13}$C in a midcontinent urban setting on a seasonal to daily basis. On average, [CO$_2$] and $\delta^{13}$C values in Evanston were 16–23 ppm higher and 0.97–1.13‰ lower than the background sites. While seasonal [CO$_2$] and $\delta^{13}$C values generally followed broader northern hemisphere trends, the difference between Evanston and the background sites was larger in winter versus summer. Mixing calculations suggest that ecosystem respiration and petroleum combustion equally contributed CO$_2$ in excess of background during the summer and that natural gas combustion contributed 80%–94% of the excess CO$_2$ in winter. Wind speed and direction strongly influenced [CO$_2$] and $\delta^{13}$C values on an hourly time scale. The highest [CO$_2$] and lowest $\delta^{13}$C values occurred at wind speeds $<3$ m s$^{-1}$ and when winds blew from the northwest, west, and south over densely populated neighborhoods.

1 Introduction

While it is clear that fossil fuel combustion and land use change are driving observed increases in global atmospheric CO$_2$ concentrations (e.g., Conway et al., 1994; Ciais et al., 1995; Keeling et al., 1995; Miller et al., 2012; Franscy et al., 2013; Tans, 2014), only 40%–50% of emitted CO$_2$ remains in the atmosphere due to uptake by oceanic and terrestrial sinks (Canadell et al., 2007; Knorr, 2009). Quantitatively modeling uptake of fossil fuel CO$_2$ by the oceanic and terrestrial sinks is challenging because seasonal changes in the biosphere (Conway et al., 1994; Miller et al., 2012), the El Nino-Southern Oscillation cycle (Keeling et al., 1995), and other phenomena drive diurnal and seasonal variations in atmospheric CO$_2$ concentrations. Quantifying the balance between various CO$_2$ sources and sinks has been done most successfully at the global and hemispheric scales, usually across annual time periods (Ciais et al., 1995; Franscy et al., 2013).

Even greater challenges exist to quantify carbon sources and sinks at regional and local scales, primarily because the processes occurring at such scales are less well-characterized. At the local scale, fewer studies...
have focused on urban centers compared to natural and agricultural systems (Peters and McFadden, 2012), in part due to the inherent complexity of urban regions. This knowledge gap is notable given that urban regions contribute ∼70% of anthropogenic CO2 emissions (Churkina, 2008) and contain the majority of the human population (53.6%, UN, 2014). Because the percentage of the global population living in urban centers is projected to increase to 66.4% by 2050 (UN, 2014), presumably with a commensurate increase in anthropogenic CO2 emissions, studies focused on urban carbon cycling are essential for more accurately predicting future climate change forcings and feedbacks. To parameterize urban carbon cycle models, it is necessary to analyze the spatial and temporal variation of local carbon sources (fossil fuel emissions and ecosystem respiration) and sinks (photosynthetic uptake) and to understand how local phenomena relate to larger regional and global trends. Establishing a comprehensive urban carbon cycle model will require data from cities and metropolitan regions representing diverse climates, population densities, and fossil fuel usage patterns (Pataki et al., 2006a; Pataki et al., 2007; Nordbo et al., 2012).

Measuring atmospheric CO2 concentrations ([CO2]) and/or CO2 fluxes at ≤1 minute intervals provides one method for quantifying carbon cycling at daily and seasonal time scales. This approach has been used for decades to study local carbon cycling in forested ecosystems (e.g., Keeling, 1958, 1961; Flanagan et al., 1996; Bowling et al., 2003; Pataki et al., 2003b; Bowling et al., 2005, 2009; Andrews et al., 2014). When collected at multiple, widely separated locations, high-frequency measurements can be employed in conjunction with model simulations to examine carbon cycling at regional to continental scales (e.g., Ciais et al., 1995; Ballantyne et al., 2011; Miller et al., 2012; Francy et al., 2013). Recently, an increasing number of studies have used high-frequency measurements to characterize urban carbon cycling (Reid and Steyn, 1997; Grimmond et al., 2002; Nemitz et al., 2002; Takahashi et al., 2002; Pataki et al., 2003a, 2006b; Vogt et al., 2006; Coutts et al., 2007; George et al., 2007; Miyaoaka et al., 2007; Bergeron and Strachan, 2011; Christen et al., 2011; Helfter et al., 2011; Rice and Bostrom, 2011; Büns and Kuttler, 2012; Contini et al., 2012; Lietzke and Vogt, 2013).

At or near the surface in urban areas, average [CO2] are typically highest in densely populated centers, lower in neighboring suburbs, and near background levels in surrounding rural areas (Idso et al., 2001; George et al., 2007; Pataki et al., 2007; Büns and Kuttler, 2012). Additionally, high [CO2] can extend 100s of meters above the surface and downwind of urban areas (Mays et al., 2009; Cambaliza et al., 2014; Turnbull et al., 2015). Both anthropogenic activity and natural processes influence seasonal and daily carbon cycles in urban ecosystems, with resulting variations in urban [CO2] and CO2 fluxes (e.g., Reid and Steyn, 1997; Grimmond et al., 2002; Pataki et al., 2007; Helfter et al., 2011). Land use also affects average [CO2] in urban areas (Henninger and Kuttler, 2010).

However, measuring [CO2] alone provides limited information about carbon sources and sinks. Net CO2 fluxes can be calculated, but contributions from fossil fuels and ecosystem processes cannot be distinguished (Turnbull et al., 2006; Miller et al., 2012). Complementary analyses of other gases, such as CO or NOx, or application of the 14C tracer, can be used to estimate CO2 contributions from fossil fuel combustion versus ecosystem respiration (Turnbull et al., 2006; Miller et al., 2012; Lopez et al., 2013). Stable carbon isotope ratios (δ13C) of CO2 can also identify contributions from photosynthesis, soil respiration, petroleum combustion, and natural gas combustion in urban areas (Clark-Thorne and Yapp, 2003; Pataki et al., 2003a; Widory and Javoy, 2003; Pataki et al., 2005, 2006b; Bush et al., 2007; Pataki et al., 2007; Newman et al., 2008; Rice and Bostrom, 2011; Wada et al., 2011; Görka and Lewicka-Szczebak, 2013; Newman et al., 2013). In most previous studies, however, the number of δ13C measurements has been constrained to several data points per day because air must be manually collected in flasks and subsequently processed through vacuum extraction or gas chromatograph systems before analysis using a gas source isotope ratio mass spectrometer (Clark-Thorne and Yapp, 2003; Pataki et al., 2003a, 2005, 2007; Newman et al., 2008; Görka and Lewicka-Szczebak, 2013). Thus, while broad patterns for urban carbon cycles have begun to emerge, long-term, continuous records for [CO2] and δ13C in urban areas are relatively scarce. In North America, continuous records of urban [CO2] that are six months or longer have only been published for Baltimore, MD, USA (George et al., 2007), Phoenix, AZ, USA (Idso et al., 2002), and Salt Lake City, UT, USA (Pataki et al., 2003a, 2007; McKain et al., 2012). Worldwide, δ13C values collected for at least six months only exist for Dallas, TX, USA (Clark-Thorne and Yapp, 2003), Los Angeles, CA, USA (Newman et al., 2008), Salt Lake City (Pataki et al., 2003a, 2007), and Wroclaw, Poland (Görka and Lewicka-Szczebak, 2013). The only published continuous record of urban [CO2] for the midcontinent of North America is from Chicago, IL, USA, for June through August, 1995 (Grimmond et al., 2002). Many factors influence urban [CO2], e.g., seasonal climate variations, ecosystem type, fossil fuel usage patterns, regional topography, and population density. Several of these factors are likely distinct for the midcontinent compared to other previously studied cities.

The advent of wavelength-scanned-cavity ring down spectrometers (WS-CRDS) now permits the simultaneous analysis of [CO2] and δ13C values at rates of >1,000 data points per day. Application of WS-CRDS is rapidly growing (Wahl et al., 2006; Rice and Bostrom, 2011; Lauvaux et al., 2012; Richardson et al., 2012; Newman et al., 2013; Sturm et al., 2013; Vogel et al., 2013). In the present study, we used a Picarro G1101-i WS-CRDS to generate a nearly continuous seven-month record for [CO2] and δ13C values for the Chicago region, which is the third largest urban center in the United States (U.S. Census Bureau, 2010). The record comprises ~2x10⁶ paired measurements, consolidated into hourly averages, and also includes complementary
meteorological data obtained from the Illinois Environmental Protection Agency and the National Weather Service. The only similar study focused on [CO₂] in Chicago was conducted in 1995 (Grimmond et al., 2002). Our dataset represents one of the longest records of [CO₂] and δ^{13}C published for any city worldwide. By incorporating information for various background locations and other cities, we use the dataset to examine how natural and anthropogenic sources of CO₂ in a midcontinent urban setting change on a seasonal to daily basis as a function of key variables, such as wind speed, wind direction, and fossil fuel usage patterns.

2 Methods

2.1 Instrumentation and sample site location

In August 2011, a Picarro G1101-i WS-CRDS was installed on the roof of Scott Hall on the Northwestern University campus in Evanston, IL (Fig. 1, N42° 03′ 06.36″, W87° 40′ 39.16″). The instrument was operated nearly continuously through February 2012. Identifying the optimal location for measuring meteorological conditions and sampling gases in urban areas involves tradeoffs (World Meteorological Organization, 2008), such as maximizing the sampling height while maintaining accessibility for equipment maintenance. Urban areas can exhibit large diurnal variations in [CO₂] (Reid and Steyn, 1997; Grimmond et al., 2002; Pataki et al., 2006b; Helfter et al., 2011; Rice and Bostrom, 2011; Büns and Kuttler, 2012). However, compared to the large range in diurnal variations, only relatively small concentration differences exist as a function of measurement height within the roughness sublayer when urban air samples are collected more than a few meters above the ground surface (Büns and Kuttler, 2012; Lietzke and Vogt, 2013). In the present study, the air intake was located on the rooftop of Scott Hall, ~18 m above street level. Scott Hall is located ~0.6 km west of Lake Michigan and sits at the intersection of two major roads (Fig. 1C). Evanston is a suburb of Chicago with 74,486 residents and a population density of 3687 persons km⁻², ~11% higher than the population-weighted density for the Chicago metropolitan area (U.S. Census Bureau, 2010). The city of Chicago, immediately south of Evanston, has ~2.7 million residents (U.S. Census Bureau, 2010). The Chicago metropolitan area contains ~9.5 million residents (U.S. Census Bureau, 2010). The Scott Hall sampling site is 3.6 km north of the Evanston–Chicago boundary and ~20 km north of downtown Chicago (Fig. 1B).

The Chicago, IL region has a continental climate with warm–hot summers and cold winters. From 1981 to February 2014, the mean annual temperature at O’Hare International Airport, ~20 km southwest of the sampling site, was 9.9°C, with average temperatures of 22.1, 11.4, and 3.1°C in the summer (June–August), fall (September–November), and winter (December–February) (National Weather Service, 2014). Average annual precipitation during the same time period was 937 mm with 306, 242, and 147 mm in the summer, fall, and winter (National Weather Service, 2014). During the study period, the average temperatures in summer, fall, and winter were 23.3, 12.2, and 0.44°C, and total precipitation was 484, 225, and 156 mm (National Weather Service, 2014).

2.2 Sampling, calibration, quality control, and data treatment

The air intake and gas transfer system was modified from a NCAR design (Stephens and Watt, 2006). A vacuum pump (KNF 811 KTP) containing a Teflon-coated diaphragm drew ambient air through a 30 μm filter attached at the inlet. Air was pumped ~10 m to a manifold using Syflex metal/plastic composite tubing with aluminum lining. Ambient air, as well as air from quality control check standards, flowed through two Nafion dryers (Perma Pure, MD–110–96F–4) before entering the instrument and then flowed out of the system through three molecular sieve dryers (Scott Specialty Gases [now Air Liquide America Specialty
Urban CO₂ concentrations and δ¹³C values from the Chicago, IL, USA region

Consequently, sample air had a low and relatively constant water content, <0.13% on average, with August–September values typically around 0.10%–0.15% and October–February values typically around 0.05%–0.10%, and the standard air was slightly humidified to the same level as sample air. Consistent water content increases the precision of WS-CRDS carbon isotope measurements (Rella, 2011). CO₂ concentrations and δ¹³C values were measured ~8 times min⁻¹.

To calibrate the instrument, two NOAA gas standards with certified CO₂ concentrations tied to the WMO scale and δ¹³C values (relative to VPDB) determined by INSTAAR at University of Colorado were analyzed ~60 times over several months (Table S1). Two check standards were repeatedly analyzed in June and July 2011 to further confirm the calibration and assess instrumental stability. The check standards were tanks of CO₂ in synthetic air (N₂ + O₂) from commercial suppliers (Airgas or Scott Specialty Gases [now Air Liquide America Specialty Gases]). During the data collection period, the NOAA gas standards were periodically analyzed to confirm the quality of the calibration. Within instrumental uncertainty, the measured [CO₂] and δ¹³C values agreed with the NOAA and INSTAAR values. Also during the data collection period, two check standards similar to the ones described above were analyzed once or twice daily, with three minutes for flushing and five minutes for measurement (Table S1). Measured [CO₂] for the check standards agreed with the supplier values and showed little evidence of drift (Table S1, Fig. S1). Flask samples were collected 0.3 m s⁻¹ (see Fig. S2).

Wind speed and direction data were collected by the Illinois Environmental Protection Agency (IL EPA) at a meteorological station located ~1.1 km from the study site (N 42°03′42.61″, W87°40′1.1″, Fig. 1C). Temperature and other weather data were recorded at O’Hare International Airport by the National Weather Service (NWS). Wind speed and direction data from O’Hare were used to fill the following intervals when the IL EPA site did not collect data: August 1, 2011 until August 9, 2011 at 14:00, and November 4 until December 8 (with the exception of November 28, 15:00 to November 29, 23:59). Wind speed and wind direction data from the NWS were reported in bins of 0.4–0.6 m s⁻¹ and 10°, respectively. The IL EPA site did not collect data: August 1, 2011 until August 9, 2011 at 14:00, and November 4 until December 8 (with the exception of November 28, 15:00 to November 29, 23:59). Wind speed and wind direction data from the NWS were reported in bins of ~0.4–0.6 m s⁻¹ and 10°, respectively. The IL EPA wind direction data were partitioned into the same bins as the NWS data. The IL EPA and the O’Hare wind directions and speeds agreed well, with O’Hare reporting a 13° bias to the west and higher wind speeds by 0.3 m s⁻¹ (see Fig. S2).

δ¹³C values were measured with the G1101-IRMS instrument at SIRFER lab at the University of Utah and δ¹³C values by IRMS in the SIRFER lab at the University of Utah (Table S1). The δ¹³C values measured with the G1101-i showed little evidence for drift beyond normal instrumental uncertainty but were 0.54‰ ± 0.15‰ (1σ) lower than those determined by IRMS (Table S1). This difference is similar to the 0.43‰ offset observed in a previous study and can be attributed to the lack of Ar in the synthetic balance air (Friedrichs et al., 2010). The NOAA standards contain Ar. Because isotopic analysis of the synthetic-air check standards was used only to monitor instrumental drift, the offset has no bearing on the measured atmospheric values.

Data reduction and analysis were performed using R (R Core Team, 2013), implemented with the standard functionality, as well as the Lubridate (Grolemund and Wickham, 2011) and Openair libraries (Carslaw and Ropkins, 2012; Carslaw, 2013). Openair was employed for atmospheric analysis and plotting, including calculation and plotting of hourly averages for diurnal plots and polar plots. Hourly averages are reported on a 24–hour period, on the basis of local time–Central Daylight Time from August to Sunday, November 6, 2011 and Central Standard Time from Sunday, November 6 to the end of the sampling period in February 2012.

2.3 Ambient meteorological data

Wind speed and direction were collected by the Illinois Environmental Protection Agency (IL EPA) at a meteorological station located ~1.1 km from the study site (N 42°03′42.61″, W87°40′1.1″, Fig. 1C). Temperature and other weather data were recorded at O’Hare International Airport by the National Weather Service (NWS). Wind speed and direction data from O’Hare were used to fill the following intervals when the IL EPA site did not collect data: August 1, 2011 until August 9, 2011 at 14:00, and November 4 until December 8 (with the exception of November 28, 15:00 to November 29, 23:59). Wind speed and wind direction data from the NWS were reported in bins of ~0.4–0.6 m s⁻¹ and 10°, respectively. The IL EPA wind direction data were partitioned into the same bins as the NWS data. The IL EPA and the O’Hare wind directions and speeds agreed well, with O’Hare reporting a 13° bias to the west and higher wind speeds by 0.3 m s⁻¹ (see Fig. S2).

2.4 Keeling plots and mixing calculations

Measured [CO₂] and δ¹³C values were used to construct Keeling plots (Keeling, 1958, 1961; Pataki et al., 2003b). As described by Pataki et al. (2003b), the measured atmospheric CO₂ concentration ([CO₂]ₐ) represents the sum of the background CO₂ concentration ([CO₂]ₐ) and the concentration of CO₂ emitted locally ([CO₂]ₗ):

\[ [CO₂]ₐ = [CO₂]ₐ + [CO₂]ₗ. \] (1)

Following the conservation of mass and the relationship between concentrations and isotope ratios (Pataki et al., 2003b), the δ¹³C value of local CO₂ sources is calculated with the equation:

\[ δ¹³Cₗ = [CO₂]ₗ (δ¹³Cₐ − δ¹³Cₗ) (1/[CO₂]ₐ) + δ¹³Cₐ, \] (2)

where δ¹³Cₐ, δ¹³Cₗ, and δ¹³Cₐ represent the carbon isotope composition of measured, local, and background CO₂, respectively. Because δ¹³Cₐ is the intercept in a linear equation, the value can be calculated from regression of δ¹³Cₗ versus 1/[CO₂]ₐ (Keeling, 1958, 1961; Pataki et al., 2003b). Ordinary least squares regression was used to construct Keeling plots (Keeling, 1958, 1961; Pataki et al., 2003b).
Urban CO₂ concentrations and δ¹³C values from the Chicago, IL, USA region used because the method introduces smaller uncertainties for calculated δ¹³Cₑ values than other regression methods (Zobitz et al., 2006).

The δ¹³Cₑ values were used to estimate relative contributions from various local CO₂ sources according to equations presented in Newman et al. (2008):

\[ f_r + f_p + f_g = 1 \]  
\[ \delta^{13}C_e = f_r \delta^{13}C_r + f_p \delta^{13}C_p + f_g \delta^{13}C_g, \]

where \( f_r \), \( f_p \), and \( f_g \) represent the fraction of [CO₂] from ecosystem respiration, petroleum combustion (almost exclusively gasoline in Evanston), and natural gas combustion, respectively, and \( \delta^{13}C_r \), \( \delta^{13}C_p \), and \( \delta^{13}C_g \) represent the corresponding carbon isotope compositions.

Data from the NOAA Ameriflux tall tower site at Park Falls, WI, USA, located ~500 km northwest of Evanston, were used to estimate background end members (Andrews et al., 2014). Average diurnal, monthly, and seasonal [CO₂] (Tables 1 and 2) were calculated from hourly [CO₂] data for the Park Falls 30 and 396 m inlets (Andrews et al., 2014). Monthly average δ¹³C values from Park Falls 396 m were used for Keeling plots and mixing calculations (White and Vaughn, 2011). Carbon isotope data are not available for Park Falls 30 m. Monthly reported [CO₂] and δ¹³C values for Mauna Loa, HI, USA (Tans, 2014) were also used to compare results from this study with previous work (Table 1). Table 2 contains literature data for average [CO₂] and δ¹³C values for other mixing end-members, namely petroleum and natural gas combustion, as well as ecosystem respiration, which includes plant and soil respiration (Bakwin et al., 1998; Widory and Javoy, 2003).

3 Results and discussion

Evanston consistently displayed higher [CO₂] and lower δ¹³C values than the background sites. Below, measurements from Evanston and the background sites are compared in progressively shorter time periods, from the entire sample period to seasonal, and finally, diurnal. The role of wind speed and direction is also discussed. Finally, seasonal variations in local CO₂ sources are quantified using Keeling plots and mass-balance mixing equations.

3.1 Average [CO₂] and δ¹³C compared to background

The average [CO₂] in Evanston from August 2011–February 2012 was 16, 20, and 23 ppm higher than the Park Falls 30 m, Park Falls 396 m, and Mauna Loa background sites, respectively (Tables 1, 3). The average [CO₂] difference between Evanston and Mauna Loa determined here is similar to the 22 ppm difference reported in a previous study conducted in Chicago during June–August, 1995 (Grimmond et al., 2002). The differences between Evanston and the background sites are in the middle of the range reported in other studies that compared urban and background [CO₂]. At the low end, [CO₂] in Portland, Oregon, USA was only ~5 ppm higher than a nearby rural area (Rice and Bostrom, 2011). Cities with [CO₂] ranging from 15–35 ppm higher than background, similar to Evanston, include Essen, Germany (Büns and Kuttler, 2012); suburban or foothill sites in Salt Lake City (Pataki et al., 2005, 2007); Tokyo, Japan (Moriwaki et al., 2006); and Vancouver, Canada (Reid and Steyn, 1997). Concentration differences of 50 ppm or more between urban and background sites were observed in densely populated sections of Los Angeles, downtown Salt Lake City, and Phoenix, all cities surrounded by mountains (Idso et al., 2001; Pataki et al., 2007; Newman et al., 2007; Nishimura et al., 2008).

Table 1. Monthly averages for background CO₂ and δ¹³C

<table>
<thead>
<tr>
<th>Month</th>
<th>Park Falls, WI - 30 m</th>
<th>Park Falls, WI - 396 m</th>
<th>Mauna Loa, HI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ (ppm)</td>
<td>δ¹³C (%)</td>
<td>CO₂ (ppm)</td>
</tr>
<tr>
<td>August 2011</td>
<td>388.8</td>
<td>nm²</td>
<td>376.3</td>
</tr>
<tr>
<td>September 2011</td>
<td>391.7</td>
<td>nm</td>
<td>386.1</td>
</tr>
<tr>
<td>October 2011</td>
<td>398.4</td>
<td>nm</td>
<td>394.3</td>
</tr>
<tr>
<td>November 2011</td>
<td>400.8</td>
<td>nm</td>
<td>399.4</td>
</tr>
<tr>
<td>December 2011</td>
<td>401.9</td>
<td>nm</td>
<td>400.6</td>
</tr>
<tr>
<td>January 2012</td>
<td>401.7</td>
<td>nm</td>
<td>400.6</td>
</tr>
<tr>
<td>February 2012</td>
<td>401.5</td>
<td>nm</td>
<td>400.7</td>
</tr>
<tr>
<td>Whole period average</td>
<td>397.9</td>
<td>nm²</td>
<td>394.0</td>
</tr>
</tbody>
</table>

² Background data are the 396 m above ground level measurements. Monthly averages were calculated from hourly data collected at the Ameriflux tall tower site at Park Falls, WI (Andrews et al., 2014).

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et al., 2008) and in densely populated Baltimore, where samples were collected only 2 m above ground level (George et al., 2007). These data suggest that the difference between urban and background [CO₂] observed in Evanston is fairly typical, although some cities have smaller or larger differences depending on the extent of local emissions, local meteorological conditions, or geological/geographic characteristics.

The average δ¹³C value in Evanston was 0.97‰ and 1.13‰ lower than Park Falls 396 m and Mauna Loa, respectively (Tables 1, 3). Several studies have reported that δ¹³C values in urban air are lower than background values (Clark-Thorne and Yapp, 2003; Pataki et al., 2003a; Widory and Javoy, 2003; Pataki et al., 2005, 2006a, 2006b, 2007; Rice and Bostrom, 2011; Górka and Lewicka-Szczebak, 2013; Lopez et al., 2013). The only previous study to report and compare average urban and background δ¹³C values over a several-month period found that urban δ¹³C values were 1.7‰ lower than background in the early 2000s (Newman et al., 2008). The Newman et al. (2008) study was conducted in Pasadena, California, USA, which receives marine air blowing directly off the Pacific Ocean, and thus, different results are expected for a midcontinent setting where seasonal changes in ecosystem productivity yield seasonal differences in δ¹³C values.

### 3.2 Seasonal [CO₂] and δ¹³C variations

Mean [CO₂] was lowest during the late summer and early fall (August–September) and highest during the winter (December–February) (Fig. 2, Table 3). The ~22 ppm difference between the [CO₂] minimum in August–September and the maximum in December–February was larger for Evanston (Table 3) than the differences for the background sites: 19, 13, and 4 ppm for Park Falls 396 m, Park Falls 30 m, and Mauna Loa, respectively (Table 1). The overall seasonal pattern for Evanston is consistent with the Park Falls background site (Table 1), as well as broader northern hemisphere [CO₂] trends, which are driven by increased photosynthesis during summer and decreased photosynthesis during winter (Lauvaux et al., 2012; Andrews et al., 2014; Tans, 2014). The seasonal pattern is also consistent with measurements made in other northern hemisphere urban areas (Pataki et al., 2003a, 2007; Kordowski and Kuttler, 2010; Helfter et al., 2011).

During the summer, [CO₂] in Evanston was ~10 ppm higher than Park Falls 30 m, which is roughly the same height as the Scott Hall station. During the winter, [CO₂] was ~20 ppm higher in Evanston. The smaller difference during summer suggests that photosynthesis and respiration strongly influence [CO₂] in both rural

### Table 2. End members for CO₂ and δ¹³C in Keeling plots

| CO₂ (ppm) | 1,000 * 1/CO₂ (ppm⁻¹) | δ¹³C (‰) | Source
|-----------|------------------------|---------|---
| Background - Park Falls, WI (396 m) | | |
| Aug-Sep 2011 | 381.1 | 26.2 | -7.89 | A |
| Oct-Nov 2011 | 396.8 | 25.2 | -8.52 | A |
| Dec 2011-Feb 2012 | 400.6 | 25.0 | -8.73 | A |
| CO₂ sources | | | |
| Natural gas | 7757.1 | 1.3 | -39.1 | B |
| Petroleum | 32340 | 0.3 | -28.7 | B |
| Respiration* | 7757.1 | 1.3 | -24.7 | C |
* Used same CO₂ concentration as petroleum.

### Table 3. Monthly averages for CO₂, δ¹³C, and meteorological data

<table>
<thead>
<tr>
<th>Month</th>
<th>CO₂ (ppm)</th>
<th>1σ</th>
<th>δ¹³C (‰)</th>
<th>1σ</th>
<th>n</th>
<th>T (°C)</th>
<th>Wind speed (m/s)</th>
<th>Wind direction (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2011</td>
<td>397.3</td>
<td>18.6</td>
<td>-8.29</td>
<td>1.0</td>
<td>680</td>
<td>23.1</td>
<td>3.01</td>
<td>314 NW</td>
</tr>
<tr>
<td>September 2011</td>
<td>402.9</td>
<td>20.3</td>
<td>-8.65</td>
<td>0.9</td>
<td>653</td>
<td>16.8</td>
<td>3.80</td>
<td>337 NNE</td>
</tr>
<tr>
<td>October 2011</td>
<td>417.8</td>
<td>23.0</td>
<td>-9.72</td>
<td>1.2</td>
<td>682</td>
<td>12.8</td>
<td>3.53</td>
<td>256 WSW</td>
</tr>
<tr>
<td>November 2011</td>
<td>414.1</td>
<td>13.4</td>
<td>-9.64</td>
<td>0.7</td>
<td>660</td>
<td>7.2</td>
<td>5.40</td>
<td>245 WSW</td>
</tr>
<tr>
<td>December 2011</td>
<td>419.0</td>
<td>12.2</td>
<td>-9.97</td>
<td>0.7</td>
<td>618</td>
<td>2.0</td>
<td>3.57</td>
<td>258 WSW</td>
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<tr>
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<td>-10.02</td>
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<td>667</td>
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Urban CO₂ concentrations and δ¹³C values from the Chicago, IL, USA region

and urban midcontinent settings, while the larger difference during winter points to the importance of urban fossil fuel emissions (see section 3.5). A similar seasonal pattern was observed in Salt Lake City, one of the few urban locations with high resolution winter data (Pataki et al., 2007).

The δ¹³C values for Evanston and the background sites inversely correlate with [CO₂], with a summer maximum and a winter minimum (Fig. 2, Tables 1, 3). As with [CO₂], the difference between summer and winter δ¹³C values was larger in Evanston and Park Falls 396 m compared to Mauna Loa. The greater amplitude of the seasonal δ¹³C variation in Evanston (1.6‰) than Park Falls 396 m (1.0‰) is also consistent with CO₂ contributions from urban fossil fuel emissions, including differing emission sources between summer and winter.

3.3 Diurnal [CO₂] and δ¹³C variations

Across the entire sampling period, average [CO₂] and δ¹³C values varied diurnally in Evanston, with low [CO₂] and high δ¹³C values in the afternoon, increasing [CO₂] and decreasing δ¹³C values during the evening, and high [CO₂] and low δ¹³C values in the early morning (Fig. 3). The average diurnal variation was ~20 ppm for [CO₂] and 1‰-1.1‰ for δ¹³C values. Evanston appears similar to other urban areas, where average [CO₂] are lowest during the daytime hours, when a relatively turbulent atmosphere mixes surface air containing local CO₂ emissions with background air containing lower [CO₂] (Reid and Steyn, 1997; Grimmond et al., 2002; Pataki et al., 2006b; Helfter et al., 2011; Rice and Bostrom, 2011; Büns and Kuttler, 2012). The same pattern also occurs in rural areas (Flanagan et al., 1996; Bowling et al., 2003, 2005). During evening through early morning hours, the [CO₂] rises because the atmosphere is generally more stable (Reid and Steyn, 1997; Grimmond et al., 2002; Pataki et al., 2006b; Helfter et al., 2011; Rice and Bostrom, 2011; Büns and Kuttler, 2012). On an hourly basis, urban CO₂ fluxes show less variation than [CO₂] (Grimmond et al., 2002) and sometimes exhibit complex patterns. For example, in some urban areas, the highest hourly CO₂ fluxes occur in the afternoon, when [CO₂] are lowest (Vogt et al., 2006; Helfter et al., 2011).

While Evanston and other urban areas exhibit diurnal variations throughout the year, the amplitude and timing of the variations change seasonally. Understanding combinations of anthropogenic and natural factors that drive seasonally-changing diurnal variations is important for elucidating why urban carbon cycles vary throughout the year. These factors are discussed in more detail in the following sections.

3.3.1 Summer diurnal variations

Summer diurnal variations for [CO₂] and δ¹³C values approached 30 ppm and 1.5‰ (Fig. 3A, 3D). The highest [CO₂] and lowest δ¹³C values occurred between 6:00 and 7:00, while the lowest [CO₂] and highest δ¹³C values occurred from 12:00-18:00 (Fig. 3A, 3D). The Park Falls 30 m background site displayed a 25 ppm diurnal range, with [CO₂] peaking in the morning and rising in the evening (Fig. 3A). CO₂ concentrations for the Park Falls 396 m site exhibited a smaller diurnal range of 5 ppm because samples were collected above the well-mixed planetary boundary layer and thus represent a larger scale, regional average. The daily average and diurnal amplitudes for [CO₂] were similar for summer weekdays and weekends (Fig. 4A). A weekday morning [CO₂] peak that occurred an hour later than the weekend peak (Fig. 4A) and a somewhat larger diurnal [CO₂] variation in Evanston compared to Park Falls 30 m are consistent with fossil fuel emissions, likely from weekday rush hour traffic.
Summer diurnal ranges observed in Evanston are similar to those reported for other northern hemisphere, mid-latitude cities. For example, the 30 ppm summer diurnal range for [CO2] in Evanston is similar to the 35 ppm diurnal range observed during the summer of 1995 in Chicago (Grimmond et al., 2002) and to the 20–30 ppm diurnal range measured in Basel, Switzerland (Vogt et al., 2006), London, England (Sparks and Toumi, 2010), Portland (Rice and Bostrom, 2011), Vancouver (Reid and Steyn, 1997), and a suburban site in Salt Lake City (Pataki et al., 2007). A morning [CO2] peak and an afternoon [CO2] low have been observed in other urban areas (e.g., Reid and Steyn, 1997; Grimmond et al., 2002; Vogt et al., 2006; Courts et al., 2007; Pataki et al., 2007; Büns and Kuttler, 2012; Contini et al., 2012; Lietzke and Vogt, 2013). In Melbourne, Australia, the only urban study from the southern hemisphere, a smaller summer diurnal range of 8–12 ppm was observed (Courts et al., 2007).

### 3.3.2 Fall diurnal variations

Fall diurnal variations were ~20 ppm for [CO2] and 1.2‰ for δ13C values (Fig. 3B, 3E). Compared to summer, the highest [CO2] and lowest δ13C values shifted later to 7:00–9:00. The shift partly reflects the change from daylight savings time to standard time, which occurred approximately halfway through the fall season. The afternoon period of low [CO2] was shorter relative to summer, and the rise toward higher evening [CO2] was steeper and began earlier, around 17:00 (Fig. 3B). Similar to summer, the fall morning [CO2] peak was synchronous with the peak recorded at the Park Falls 30 m site, but the late afternoon [CO2] rise in Evanston was earlier and more rapid (Fig. 3B).

While fall weekdays and weekends displayed the same average daily [CO2] within uncertainty, average hourly [CO2] for weekdays was higher than weekends from 11:00 to 19:00, and the late afternoon [CO2] rise was earlier and more abrupt on weekdays (Fig. 4B). Higher hourly [CO2] during the midday and late afternoon suggest contributions from local vehicular traffic. The late afternoon [CO2] increase likely reflects emissions during the evening rush hour (Fig. 4B). Based on 2010 measurements, average traffic volumes from three nearby measurement locations—the Evanston intersection where sampling occurred and two adjacent

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**Figure 3**

Diurnal variations in CO2 concentrations and δ13C values for each season.

Hourly mean values for CO2 concentrations ([CO2]) and δ13C values during (A, D) summer, (B, E) fall, and (C, F) winter. [CO2] averages shown in grey are background measurements from 30 m height at the background site in Park Falls, WI, USA for (A) summer, (B) fall, and (C) winter. The bold line shows hourly means, and the shaded regions represent 95% confidence intervals. Evanston [CO2] increases, and δ13C values decrease, from summer to winter. The amplitude of the average diurnal variation in Evanston decreases from summer to winter. [CO2] at the background site also increases from summer to winter, although to a smaller degree. Average diurnal variations for Evanston and Park Falls are similar in the summer (25–30 ppm) but much different in the winter: ~15 ppm for Evanston and <1.25 ppm for Park Falls.

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**Figure 4**

Weekday versus weekend diurnal variations in CO2 concentrations for each season.

Hourly mean CO2 concentrations ([CO2]) for weekday (red) versus weekends (grey) for (A) summer, (B) fall, and (C) winter. The bold line shows hourly means, and the shaded regions represent 95% confidence intervals. In the summer, weekday and weekend hourly averages are indistinguishable. In the fall and winter, weekday hourly averages are higher than weekend averages.

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intersections located north and south of the sampling site—were 13,545 vehicles day$^{-1}$, with 24% (3260 vehicles) of the daily traffic occurring from 16:00–19:00 (Illinois Department of Transportation, 2010). These vehicle counts are likely minimum estimates because the data were collected during the summer when Northwestern University was out of session, resulting in less traffic than during the academic year. The late afternoon [CO$_2$] increase in Evanston was not evident during the summer (Fig. 3A, 4A), which could reflect several factors, including longer periods of daylight causing photosynthetic activity to continue through the early evening, a longer duration of atmospheric mixing, and less activity at the university compared to the academic year. The suggestion that photosynthetic drawdown of CO$_2$ during the summer can be large enough to mask the evening rush hour signal highlights the significance of local plant growth in urban carbon cycling. Some studies attributed afternoon [CO$_2$] increases to the end of the day rush hour (Lietzke and Vogt, 2013; Newman et al., 2013), whereas others did not observe an afternoon increase (Reid and Steyn, 1997; McKain et al., 2012). Because afternoon [CO$_2$] increases are relatively small, their detection partly depends on measurement height. For example, in Basel, an afternoon increase was observed for measurements taken at 3 and 19 m above ground level but not at 39 m above ground level, where air is more well-mixed (Lietzke and Vogt, 2013).

### 3.3.3 Winter diurnal variations

Winter diurnal variations were ~15 ppm for [CO$_2$] and 1% for δ$^{13}$C values (Fig. 3C, 3F). Average daily [CO$_2$] for weekdays was 2.7 ppm higher than weekends. Average hourly [CO$_2$] was higher during weekdays than weekends during the time period 5:00–13:00 (Fig. 4C). Similar to the fall, the late afternoon [CO$_2$] rise in winter was more abrupt during weekdays (Fig. 4C). About 42% of the total daily traffic passed during morning and afternoon rush hours: 2453 vehicles (18%) from 7:00–10:00 and 3260 vehicles (24%) from 16:00–19:00 (Illinois Department of Transportation, 2010). In contrast to Evanston, winter diurnal variations observed at both Park Fall sites were <1.25 ppm (Fig. 3C). The small diurnal variation at Park Falls demonstrates minimal CO$_2$ contributions from ecosystem respiration, as expected for the winter season. The larger diurnal variations in Evanston compared to Park Falls therefore point to fossil fuel emissions as the major source of CO$_2$. The increase in [CO$_2$] from 0:00–6:00 almost certainly reflects natural gas emissions from building heating because vehicular traffic was low. Only ~360 vehicles, or 2.6% of the daily total traffic, passed during this time (Illinois Department of Transportation, 2010). The timing and size of the weekday versus weekend morning peaks in Evanston (Fig. 4A, 4C), as well as the similarity of the summer and fall morning peaks in Evanston and Park Falls but near absence of a winter morning peak at Park Falls (Figs. 3A–C), collectively suggest that local ecosystem respiration controls much of the size and timing of morning [CO$_2$] in summer and that fossil fuel emissions control the morning [CO$_2$] peak in winter.

The winter diurnal range in Evanston is similar to the 15–20 ppm diurnal range observed at several other northern hemisphere urban sites, such as Basel (Lietzke and Vogt, 2013); Essen (Büns and Kuttler, 2012); Lecce, Italy (Contini et al., 2012); and London (Sparks and Touni, 2010). Similar to fall and winter patterns in Evanston, weekday peaks in Basel occurred later and were larger than weekend peaks (Lietzke and Vogt, 2013). Suburban and downtown sites in Salt Lake City exhibited average winter diurnal variations of 25–30 ppm and 40–50 ppm, respectively (Pataki et al., 2007). The larger diurnal variations recorded for Salt Lake City likely reflect the influence of mountains, which surround the city and reduce atmospheric mixing (Pataki et al., 2005).

Both urban and background sites exhibit diurnal variations, with the amplitude and timing changing seasonally. However, diurnal ranges are consistently larger in Evanston compared to the background sites, especially during the winter. The seasonal pattern of diurnal variations in Evanston is similar to the patterns documented for many other northern hemisphere cities. While local factors, like topography for Salt Lake City, can impact diurnal variations, the overall similarity between Evanston and other northern hemisphere cities suggests common controlling variables, such as meteorological conditions and seasonal changes in natural versus fossil fuel [CO$_2$] sources. These factors are discussed in more detail in the following two sections.

### 3.4 $[CO_2]$ as a function of wind speed and direction

Although considerable variation exists, the highest [CO$_2$] generally occurred at the lowest wind speeds regardless of season (Fig. 5A). As wind speeds increased, the concentration and extent of variation decreased. Daily variations in wind speed (horizontal advection of air) and the thickness of the well-mixed planetary boundary layer (vertical mixing) strongly influenced [CO$_2$] and δ$^{13}$C values (Fig. 3, 5A). For example, from 12:00 to 16:00, mean [CO$_2$] was lowest (Fig. 3) while wind speed was highest (4.30 m s$^{-1}$ on average). In contrast, from 03:00–07:00, [CO$_2$] was highest (Fig. 3) while mean wind speed was lowest (3.44 m s$^{-1}$ on average). The thickness of the well-mixed layer also affects [CO$_2$] by changing the fraction of the atmosphere that receives direct inputs of CO$_2$ emissions from the surface. In urban areas, the thickness of the well-mixed layer increases from sunrise until early to mid-afternoon and then decreases to a minimum at night (Helfter et al., 2011; Strong et al., 2011; Newman et al., 2013). In four cities located in, or around, the midwestern US, the thickness of the well-mixed layer was 300–500 m in the morning and 1700–1900 m in the afternoon (Holzworth, 1967). As the thickness of the well-mixed layer increases, low [CO$_2$] air from higher in
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the atmosphere can be entrained, thereby lowering locally measured [CO₂] (Holzworth, 1967; Strong et al., 2011). This type of diurnal relationship between [CO₂] and atmospheric mixing is common in both urban and rural areas (e.g., Flanagan et al., 1996; Reid and Steyn, 1997; Grimmond et al., 2002; Bowling et al., 2003, 2005; Vogt et al., 2006; Coutts et al., 2007; Büs and Kuttler, 2012).

Wind direction is also a critical factor. The correspondence between hourly [CO₂] and wind direction demonstrates that CO₂ emissions from nearby populated areas contributed to high [CO₂]. In Evanston, densely populated areas are located to the northwest, west, and south, whereas Lake Michigan is located to the east and north (Fig. 1). Higher [CO₂] occurred when winds blew from the west or south (Fig. 5B). Lower concentrations dominated when winds blew from the east or north over Lake Michigan (Fig. 5B). When winds blew from the west-northwest to southwest, [CO₂] was highest at night and early morning (21:00 to 08:00) and lowest during the day (Fig. 5B). When winds blew from the east to southeast, the lowest concentrations occurred during the evening or midday (Fig. 5B). One exception occurred during the midday, when winds blew from the southeast over the nearby intersection of two major roads and the population center of Chicago.

Fundamental patterns emerge when [CO₂] is examined as a function of both wind speed and direction. Figure 6 provides a polar plot, where mean [CO₂] is plotted for each vector of wind speed and wind direction (Carslaw and Ropkins, 2012; Carslaw, 2013). The overall pattern with wind speed and direction was consistent across each of the three seasons (Fig. S3). Local [CO₂] was at, or above, the average concentration for the entire measurement period when winds blew from the south to southwest at speeds of 10 m s⁻¹ or less, or from the west at speeds of 7 m s⁻¹ or less (Fig. 6). Additional small regions yielding above average concentrations were seen to the north-northwest and northeast at higher wind speeds (8–12 m s⁻¹, Fig. 6). The higher concentrations to the north-northwest likely reflect winds blowing over nearby neighborhoods and suburbs. Higher concentrations were recorded when winds blew from the northeast at velocities of 9–14 m s⁻¹ (Fig. 6), which could reflect CO₂ emissions from the Northwestern University steam plant, ~0.45 km northeast of the sampling site (Fig. 1). In 2010, the plant had a capacity of 180 million BTU hour⁻¹ in the most commonly used boiler and 125 million BTU hour⁻¹ in secondary boilers that supplemented output during high demand periods, especially during winter (personal communication, Northwestern University Facilities and Maintenance). Based on estimates of the total CO₂ emissions within Evanston (City of Evanston, 2008) and the US Energy Information Administration coefficient of 53.2 kg CO₂ emitted per million BTU for natural gas, the steam plant emits 17%–26% of the CO₂ within the Evanston borders.

3.5 CO₂ sources and sinks

Keeling plots showing δ¹³C values versus 1/[CO₂] were used to estimate the fraction of CO₂ contributed from fossil fuel and plant respiration sources. Summer data plot between the mixing lines for ecosystem respiration and petroleum combustion (Fig. 7A). Local CO₂ drawdown and attendant carbon isotope fractionation by photosynthesis clearly occurred during summer, as many δ¹³C values are more positive than the background value (Fig. 7A). Fall and winter data plot between the mixing lines for petroleum and natural gas combustion, with fall data plotting closer to the petroleum line and winter data plotting closer to the natural gas line (Figs. 7B and 7C). Several studies have identified local fossil fuel CO₂ emissions as the likely source of low δ¹³C values measured for urban CO₂ (Clark-Thorne and Yapp, 2003; Pataki et al., 2003a; Widory and Javoy, 2003; Pataki et al., 2005, 2006a, 2006b, 2007; Rice and Bostrom, 2011; Górk’a and Lewicka-Szczebak, 2013; Lopez et al., 2013).
The $1/[\text{CO}_2]_L$ and $\delta^{13}C$ values highly correlate for multiple time periods, including each season, afternoon hours (12:00 –16:00), and night hours (00:00–06:00 local time) (Table 4). Afternoon values for the slope and intercept are the same within statistical uncertainty across the sampling period. From summer to winter, the slope of the best–fit line became steeper, and the y-intercept, $\delta^{13}C_L$, became more negative by 7‰ (Table 4, Fig. 7). The nighttime data reflect periods when the well-mixed layer was at its lowest elevation and advective transport was minimal. Several studies have used the $\delta^{13}C_L$ from nighttime data to determine the $\delta^{13}C$ value of ecosystem respiration (Pataki et al., 2003b; Zobitz et al., 2006; Bowling et al., 2009) and to determine CO$_2$ sources in urban areas (Pataki et al., 2003a, 2006b, 2007). Similarly, we used nighttime data to determine the $\delta^{13}C_L$ value for local CO$_2$ sources representing a mixture of ecosystem respiration and fossil fuel emissions. Given that the Evanston dataset represents the longest continuous $\delta^{13}C$ record yet published, with hundreds of nighttime data points for each season, the estimated $\delta^{13}C_L$ values are likely robust.

Simple mixing model scenarios were used to constrain contributions from ecosystem respiration and different fossil fuel sources in the summer and winter seasons (Table 5). Both ecosystem respiration and building heating likely contributed CO$_2$ during the fall. Therefore, we were unable to make simplifying assumptions necessary for computing mixing model scenarios for this season. The summer and winter scenarios were used to bracket the combinations of fossil fuel emissions and respiration inputs that reasonably reproduce the

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<th>$\delta^{13}C_L$ (intercept)</th>
<th>1 σ</th>
<th>$R^2$</th>
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$^a$ Winds from 0–180 degrees

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measured δ13C values. Note that the statistical uncertainty of the linear regression (0.2‰–0.4‰) used to determine δ13C values yields a 3%–5% uncertainty in the contributions of different CO2 sources (Table 5).

For the summer, scenarios 1–5 show the respiration contribution across a range of fossil fuel contributions from 100% natural gas to 100% petroleum (Table 5). In scenarios 1–4, ecosystem respiration contributes at least 48.5% to δ13C. However, scenario 1 and 2 are unlikely because the estimates for natural gas usage are too high for summer, yet scenario 5 also seems unlikely because even during summer, some natural gas combustion is necessary for heating water, particularly on campus and in dense residential areas surrounding the sampling location. Given that natural gas demand is relatively low during warm months, scenario 4, and to a lesser extent, scenario 3, are the most plausible, with plant respiration contributing 48.5%–63% to δ13C (Table 5). An uncertainty of <15% seems reasonable given that uncertainties can exceed 30% in cases where a single source does not contribute at least 70% of the local CO2 (Pataki et al., 2007).

The summer contribution from ecosystem respiration in Evanston lies at the middle of the range estimated for other cities using δ13C, as well as CO and 14C. On the low end, respiration contributed 20%–30% of the excess CO2 during late spring in Nagoya, Japan (Wada et al., 2011) and 35%–50% in late summer in Salt Lake City (Pataki et al., 2007). Respiration in the Los Angeles basin has been estimated to be as low as 50% during the late spring (Newman et al., 2013) and as high as 75% for a mid-spring day at the end of the local rainy season (Djuricin et al., 2010). Evanston was similar to Dallas and Salt Lake City, in that petroleum combustion was the major fossil fuel contributor in the summer (Table 5, Clark-Thorne and Yapp, 2003; Pataki et al., 2007).

In winter, the ecosystem respiration component was almost certainly ≤20% and likely 0%–10% (Table 5). When ecosystem respiration is modeled as 30% in winter (scenario 4), then the modeled nighttime δ13C value was 0.9‰ more positive than the measured value (Table 5). Low respiration is consistent with low winter nighttime δ13C values from the Chicago, IL, USA region.

Table 5. Scenarios for contributions of ecosystem respiration & fossil fuel CO2 sources

<table>
<thead>
<tr>
<th>Month</th>
<th>Measured nighttime δ13C value (%)</th>
<th>Fossil fuel δ13C value (%)</th>
<th>Petroleum contribution (%)</th>
<th>Natural gas contribution (%)</th>
<th>Total fossil fuel contribution (%)</th>
<th>Ecosystem respiration contribution (%)</th>
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</thead>
<tbody>
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<td>Summer</td>
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<td></td>
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<td>25.0</td>
<td>75.0</td>
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<td>-39.1</td>
<td>0.0</td>
<td>100.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>

b Based on mixing of fossil fuel δ13C values from Table 2.
temperatures, which slow metabolic processes. Diurnal [CO₂] variations for Park Falls 30 m were only ~1 ppm for the same period, which provides additional evidence for minimal respiration (Fig. 3C). Thus, the Evanston winter CO₂ end member was dominated by contributions from local petroleum and natural gas combustion rather than respiration (Table 5). The signal from fossil fuel combustion in densely populated areas to the west and south can be seen by comparing the overall average winter nighttime δ¹³C, value of ~35.7‰ with the δ¹³C, value of ~32.2‰ when winds blew from the east over Lake Michigan (0–180 degrees, Table 4). Air coming from the direction of Lake Michigan contains less CO₂ from fossil fuel emissions, resulting in a more positive δ¹³C, value. In winter, natural gas combustion contributed more than 67% of the excess CO₂ in scenario 1 with no respiration and 76% in scenario 2 where respiration constituted 10% of the high [CO₂] end member (Table 5). Scenario 3 is unlikely because the contribution of petroleum combustion to local CO₂ almost certainly exceeds 6%, given the estimated results for summer. Large contributions from natural gas combustion occurred during winter, even though the temperature was slightly warmer than average, 0.44°C for the study period versus ~3.1°C from 1981–2014 (National Weather Service, 2014). Scenarios suggesting large natural gas contributions during the winter and modest contributions during the summer are generally consistent with an emissions inventory for the broader Chicago region, where annual greenhouse gas emissions (primarily CO₂) from natural gas usage were ~50% higher than emissions from the transportation sector (McGraw et al., 2010). Similarly, a greenhouse gas inventory for Evanston found that emissions from natural gas combustion were 2.7 times higher than emissions from gasoline or diesel combustion (City of Evanston, 2008). The scenarios are also consistent with CO₂ emissions estimates based on fuel consumption for the approximate latitude and longitude of Chicago, which indicate that emissions from natural gas combustion vary by ~70%–80% between summer and winter, while emissions from petroleum combustion vary by <10% (Gregg et al., 2009). The net result is that overall emissions are highest during winter months and that natural gas combustion is the largest source (Gregg et al., 2009).

Our estimates for winter ecosystem respiration in Evanston are similar to other northern cities where winter temperatures are cold enough to require building heating: 11% in Nagoya, Japan (Wada et al., 2011), 5%–30% in Salt Lake City (Pataki et al., 2007), and 20%–30% in Paris, France (Lopez et al., 2013). Like Evanston, natural gas was the major fossil fuel contributor in the winter in Salt Lake City (Pataki et al., 2006b, 2007) and Paris (Lopez et al., 2013). In Wroclaw, carbon isotope data revealed that coal was the major fossil fuel contributor in the winter (Górka and Lewicka-Szczebak, 2013). Evanston respiration values are lower than the 52%–66% estimated for Los Angeles (Djuricin et al., 2010), which is expected given that warmer temperatures and seasonally higher rainfall in Los Angeles support plant growth in the winter. In Los Angeles and Portland, the winter contribution from petroleum combustion was 25%–50% higher than the contribution from natural gas combustion (Djuricin et al., 2010; Rice and Bostrom, 2011). In Los Angeles, winter natural gas usage is low by comparison to Evanston, and the Portland study did not consider ecosystem respiration. Clearly, climate, extent of vegetation cover, and local energy infrastructure affect the relative contributions of ecosystem respiration and fossil fuels to urban carbon cycles, with seasonal variations expected for cities located in temperate climates.

4 Conclusions

This study employed a Picarro G1101-i WS-CRDS to generate nearly continuous records for the concentration and carbon isotope composition (δ¹³C) of atmospheric CO₂ in Evanston, IL for the time period August 2011 through February 2012. Evanston is adjacent to Chicago, IL, which is the third largest city in the US. Evanston displayed high [CO₂] and low δ¹³C values compared to background sites in Park Falls, WI, and Mauna Loa, HI. Similar to previous studies conducted in other urban areas (Clark-Thorne and Yapp, 2003; Pataki et al., 2006b, 2007; Lietzke and Vogt, 2013), the patterns for Evanston reflect the combined influence of natural and anthropogenic factors, especially ecosystem respiration and local fossil fuel CO₂ emissions.

While overall seasonal variations in [CO₂] and δ¹³C largely followed broader midcontinental trends, relatively large amplitude shifts in local δ¹³C values point to seasonally changing CO₂ sources in Evanston. Similarities in the timing and size of average diurnal fluctuations in [CO₂] for Evanston and Park Falls during the summer suggest that ecosystem respiration influenced [CO₂] in Evanston. Larger average diurnal [CO₂] fluctuations in Evanston compared to Park Falls during fall and winter point to the importance of local fossil fuel CO₂ emissions. In particular, relatively high [CO₂] and low δ¹³C values measured during the fall and winter suggest elevated contributions from natural gas combustion.

On any given day, a combination of local natural CO₂ cycling, anthropogenic activity, and atmospheric conditions controlled [CO₂] and δ¹³C values. For hourly and daily periods, wind speed and direction strongly influenced atmospheric [CO₂] and δ¹³C values. The highest [CO₂] and lowest δ¹³C values were observed at wind speeds <3 m s⁻¹ and when winds blew from the northwest, west, and south over densely populated areas. Also, a large local CO₂ source, the Northwestern University central steam plant, was detectable when wind blew from the northeast, forcing emissions from the plant toward the measurement site.

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Keeling plots were used to constrain seasonally changing CO2 sources. In summer, nighttime measurements suggest that local ecosystem respiration contributed 50%–60% of the CO2 in excess of background and that fossil fuel combustion, primarily petroleum combustion, contributed the remainder. In winter, ecosystem respiration only contributed 0%–10% of the excess CO2 and fossil fuel emissions, primarily natural gas combustion, contributed the remaining 90%–100%. This study confirms the utility of δ13C for estimating ecosystem and fossil fuel contributions to urban CO2. Overall, the seasonal pattern in Evanston/Chicago is similar to that observed for other northern hemisphere, mid-latitude cities where local vegetation provides a CO2 sink and source during summer and fossil fuel emissions, from natural gas in the case of Evanston, dominate CO2 contributions during winter.

References


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**Contributions**

- Contributed to conception and design: JM, ADJ
- Contributed to acquisition of data: JM
- Contributed to analysis and interpretation of data: JM, ADJ
- Drafted and/or revised the article: JM, ADJ
- Approved the submitted version for publication: JM, ADJ

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Competing interests
The authors do not have any competing interests.

Supplemental material

• Table S1. CO₂ concentration and δ¹³C value calibration and check standard data. doi: 10.12952/journal.elementa.000052.s001

• Figure S1. Time series of CO₂ concentrations and δ¹³C values for check standards.
CO₂ concentrations and δ¹³C values versus time for (A) and (B) low check standards and (C) and (D) high check standards. Solid lines represent the average and the dashed lines denote 1σ uncertainties. doi: 10.12952/journal.elementa.000052.s002

• Figure S2. Frequency plot of differences in wind direction and speed between weather stations.
Frequency plot of differences in wind direction and speed between the Illinois Environmental Protection Agency (IL EPA) and National Weather Service at O’Hare International Airport (NWS), where the length of the red bars represents how frequently NWS wind speeds were faster than the IL EPA wind speeds, and the length of the blue bars represents how frequently the NWS wind speeds were slower than the IL EPA wind speeds. The orientation of the bars represents the directional bias of the NWS dataset relative to the IL EPA dataset. Overall, relative to the IL EPA dataset, NWS wind speeds were 0.3 m s⁻¹ faster, and the NWS mean wind direction was biased 13.3° to the west. doi: 10.12952/journal.elementa.000052.s003

• Figure S3. Seasonal polar plots with mean CO₂ concentrations as a function of wind direction and speed.
Polar plots of CO₂ concentrations ([CO₂]) versus wind speed and direction for (A, D) summer, (B, E) fall, and (C, F) winter. Each pixel represents the mean [CO₂] for a given wind speed and direction. The wind speed increases with distance from the center. The white areas represent wind speed and directions with little or no data. The polar plots are displayed in two different ways: centered around the [CO₂] average for each season (A–C) or centered around the [CO₂] average for the entire period (D–F). The pattern of [CO₂] versus wind direction and speed for each season looks quite similar to the pattern for the entire period. doi: 10.12952/journal.elementa.000052.s004

Data accessibility statement
The NOAA CO₂ concentration and δ¹³C values used in this study are publicly available from the NOAA or Ameriflux websites. The climate data are publicly available from the National Weather Service and from the Illinois Environmental Protection Agency. The CO₂ concentrations and δ¹³C values generated in this study along with the compiled meteorological data are available from the Dryad Digital Repository: http://dx.doi.org/10.5061/dryad.h8d0n.

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