Toward quantification and source sector identification of fossil fuel CO\textsubscript{2} emissions from an urban area: Results from the INFLUX experiment

Jocelyn C. Turnbull\textsuperscript{1,2}, Colm Sweeney\textsuperscript{2,3}, Anna Karion\textsuperscript{2,3}, Timothy Newberger\textsuperscript{2,3}, Scott J. Lehman\textsuperscript{4}, Pieter P. Tans\textsuperscript{5}, Kenneth J. Davis\textsuperscript{2}, Thomas Lauvaux\textsuperscript{5}, Natasha L. Miles\textsuperscript{5}, Scott J. Richardson\textsuperscript{6}, Maria Obiminda Cambaliza\textsuperscript{6}, Paul B. Shepson\textsuperscript{6}, Kevin Gurney\textsuperscript{7}, Risa Patarasuk\textsuperscript{7}, and Igor Razlivanov\textsuperscript{7}

\textsuperscript{1}National Isotope Centre, GNS Science, Lower Hutt, New Zealand, \textsuperscript{2}CIRES, University of Colorado at Boulder, Boulder, Colorado, USA, \textsuperscript{3}NOAA/ESRL, Boulder, Colorado, USA, \textsuperscript{4}INSTAAR, University of Colorado at Boulder, Boulder, Colorado, USA, \textsuperscript{5}Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania, USA, \textsuperscript{6}Department of Chemistry, Purdue University, West Lafayette, Indiana, USA, \textsuperscript{7}School of Life Sciences, Arizona State University, Tempe, Arizona, USA

Abstract The Indianapolis Flux Experiment (INFLUX) aims to develop and assess methods for quantifying urban greenhouse gas emissions. Here we use \textsuperscript{13}CO\textsubscript{2} and CO measurements from tall towers around Indianapolis, USA, to determine urban total CO\textsubscript{2}, the fossil fuel derived CO\textsubscript{2} component (CO\textsubscript{2,ff}), and CO enhancements relative to background measurements. When a local background directly upwind of the urban area is used, the wintertime total CO\textsubscript{2} enhancement over Indianapolis can be entirely explained by urban CO\textsubscript{2,ff} emissions. Conversely, when a continental background is used, CO\textsubscript{2,ff} enhancements are larger and account for only half the total CO\textsubscript{2} enhancement, effectively representing the combined CO\textsubscript{2,ff} enhancement from Indianapolis and the wider region. In summer, we find that diurnal variability in both background CO\textsubscript{2} mole fraction and covarying vertical mixing makes it difficult to use a simple upwind-downwind difference for a reliable determination of total CO\textsubscript{2} urban enhancement. We use characteristic CO\textsubscript{2,ff} source sector CO:CO\textsubscript{2} emission ratios to examine the contribution of the CO\textsubscript{2,ff} source sectors to total CO\textsubscript{2}ff emissions. This method is strongly sensitive to the mobile sector, which produces most CO. We show that the inventory-based emission product (“bottom up”) and atmospheric observations (“top down”) can be directly compared throughout the diurnal cycle using this ratio method. For Indianapolis, the top-down observations are consistent with the bottom-up Hestia data product emission sector patterns for most of the diurnal cycle but disagree during the nighttime hours. Further examination of both the top-down and bottom-up assumptions is needed to assess the exact cause of the discrepancy.

1. Introduction

Emissions of fossil fuel-derived carbon dioxide (CO\textsubscript{2,ff}) are the main driver of the postindustrial increase in atmospheric CO\textsubscript{2} mole fraction [e.g., Conway \textit{et al.}, 2011]. Knowledge of the sources and magnitude of CO\textsubscript{2,ff} emissions are critical to improving our understanding of Earth’s carbon cycle and climate system. Urban emissions are of particular interest, because urban areas currently account for ~75% of global CO\textsubscript{2,ff} emissions [\textit{World Bank}, 2010; \textit{International Energy Agency}, 2008], and by 2050, the global urban population is expected to grow from the current 3.6 billion to roughly 6 billion [\textit{United Nations Department of Economic and Social Affairs}, 2012]. Cities are often leading the way in attempts to monitor and reduce emissions, and details of emissions from individual source sectors are needed to allow policymakers to implement and verify emission-reduction strategies.

The CO\textsubscript{2,ff} emission flux is typically determined using “bottom-up” inventory methods, whereby reported fossil fuel usage from each source sector is convolved with the estimated carbon content of each fuel type to obtain CO\textsubscript{2,ff} emission flux estimates. At the national and annual scale, CO\textsubscript{2,ff} emission estimates likely have an uncertainty of between 3 and 40%, varying widely by country and reporting method [Marland \textit{et al.}, 2009]. Bottom-up methods are also using new techniques and data sets to try to quantify emissions at increasingly smaller scales. Recent efforts at the urban domain level estimate emissions at the hourly time scale and for individual buildings, road segments, and point sources [Gurney \textit{et al.}, 2009, 2012]. Uncertainties are not
well known at these spatial and temporal scales, in part because the reported emissions are often disaggregated using ancillary information. For example, vehicle emissions are estimated from activity data (vehicle miles traveled) at the monthly or annual scale, and traffic monitoring is sometimes used to estimate finer temporal and spatial resolution. Residential fossil fuel use, such as from natural gas or fuel oil home heating, may be estimated from fuel consumption at the U.S. county scale and disaggregated using building energy modeling and building survey data. These bottom-up emissions consider only emissions that actually occur in the region of interest and do not consider indirect emissions such as those due to production of imported goods or electricity generated elsewhere.

As CO₂ff emissions become regulated and a market value is associated with these emissions, rigorous, verifiable quantification of emissions requiring multiple methodologies will be needed [Tans and Wallace, 1999]. Atmospheric “top-down” approaches are complementary to the more widely used bottom-up methods. In the most direct top-down method, atmospheric measurements of the CO₂ff mole fraction are combined with information about atmospheric transport to determine CO₂ff emissions with quantifiable uncertainties [e.g., Levin et al., 1989; van der Laan et al., 2010; Turnbull et al., 2011a]. Comparison of top-down and bottom-up methods allows testing and improvement of both methods, and provides the opportunity to create integrated top-down and bottom-up emissions quantification systems that can quantify both the total emissions, trends, and the detailed spatial, temporal, and source sector patterns of emissions that are needed for policy relevance.

Top-down greenhouse gas (GHG) measurements from urban areas are a relatively new research area, and optimal sampling strategies are not yet clear. Of particular importance is the ability to isolate the local urban emissions from regional signals, for which the choice of background constraint will be critical. Another major challenge in the top-down method is to securely isolate and quantify the CO₂ff mole fraction contributed by local urban emissions. The radiocarbon content of CO₂ (¹⁴CO₂) is a highly effective method of isolating recently added (local or regional) CO₂ff from other CO₂ sources and sinks, mainly biospheric exchange (CO₂bio), which we consider to include biomass and biofuel burning as well as photosynthesis and respiration [Turnbull et al., 2006]. However, ¹⁴CO₂ measurement methods require collection and processing of air samples in a laboratory setting, limiting the number of ¹⁴CO₂ measurements that can be made. Thus, proxies for CO₂ff are frequently needed in order to augment ¹⁴CO₂ measurements and increase the temporal and spatial resolution of available CO₂ff observations.

Since CO₂ff is likely the dominant CO₂ source from an urban area, it is sometimes assumed that the CO₂ enhancement over background (ΔCO₂) is entirely due to urban CO₂ff emissions [e.g., Mays et al., 2009; Lauvaux et al., 2013]. Yet while CO₂ff is the largest net CO₂ flux to the atmosphere on the annual time scale, CO₂ exchange with the terrestrial biosphere (CO₂bio) dominates seasonal and diurnal variability in CO₂ over the continents [e.g., Miles et al., 2012]. Urban areas may have weaker CO₂bio exchange than rural or undeveloped regions, but some CO₂bio contribution is still to be expected [e.g., Pataki et al., 2006; Hutyra et al., 2011; Turnbull et al., 2011a]. Isolating the urban CO₂ff signal from this large and varying CO₂bio signal is critical.

Carbon monoxide (CO) has been widely used as a proxy tracer for CO₂ff [e.g., Meijer et al., 1996; Potosnak et al., 1999; Levin and Karstens, 2007; Dijurcin et al., 2010; Vogel et al., 2010; Newman et al., 2013]. CO is emitted during incomplete combustion, with the CO emission rate dependent on the fuel carbon content and combustion conditions. In this method, the CO:CO₂ff emission ratio (R₂CO) is determined empirically from ¹⁴CO₂-constrained estimates of CO₂ff and CO measurement observations for a given source type or location and time period [Turnbull et al., 2011a; Levin and Karstens, 2007]. In some cases, R₂CO has been assumed from other sources such as bottom-up inventory data [Potosnak et al., 1999] or the empirically derived emission ratio has been adjusted for estimated temporal variability [Vogel et al., 2010]. R₂CO is then applied to higher resolution CO measurements to provide a more complete temporal and/or spatial pattern of the CO₂ff mole fractions. An important caveat for this method is that different CO₂ff source sectors can have widely differing R₂CO, so that in an urban area with heterogeneous emission sources and temporal variability in those emissions, it may be difficult to robustly assign an appropriate emission ratio. This leads to the possibility that characteristic source sector R₂CO ratios could instead be used to partition CO₂ff emissions by source sector.

The Indianapolis Flux Experiment (INFLUX) experiment involves continuous and flask sampling of GHGs, ancillary trace gases, and their isotopes from 12 towers situated throughout the greater Indianapolis area, as well as periodic aircraft sampling. Additional measurements including Fourier transform infrared, light detection and
ranging, and meteorological measurements have recently been added. A high-resolution bottom-up estimate of Indianapolis CO$_2$ff emissions is provided by the Hestia data product [Gurney et al., 2012]. The focus of this paper is on continuous and flask measurements of CO$_2$, CO, and $^{14}$CO$_2$ (flask only, as a proxy for CO$_2$ff) from the INFLUX tower network. We first use this large tower network to examine how the choice of sampling location influences the results, focusing in particular on the choice of background sampling location. Next, we consider how well the CO$_2$ enhancement approximates the CO$_2$ff enhancement for the urban area. Then, we use the CO$_2$ enhancement and $R_{CO}$ to examine the relative contributions of the CO$_2$ff source sectors to total CO$_2$ff emissions, throughout the diurnal cycle, comparing our top-down atmospheric observations with bottom-up estimates derived from the Hestia data product. Finally, we discuss in our conclusions how our results might be used to inform sampling strategies for other urban areas.

2. Methods

2.1. Sampling Locations and Methods

Indianapolis, IN, USA, was chosen as a test case since it is a relatively isolated urban area surrounded by cropland (Figure 1). The flat terrain makes dispersion modeling and interpretation relatively simple. The city of Indianapolis had estimated CO$_2$ff emissions of ~3.3 MtC yr$^{-1}$ in 2012, making it the eleventh largest city in the United States in terms of CO$_2$ff emissions [Gurney et al., 2012]. Gurney et al. [2012] examined the source distribution of Indianapolis CO$_2$ff emissions for the year 2012, showing that emissions come from a variety of different sources, including 44% from vehicles (on-road, off-road, railroads, and airport sources), 29% from the large coal-fired Harding Street Power Plant (HSPP) located near the center of the city, and the remaining 27% from the commercial, industrial, and residential sectors (e.g., emissions from heating and industrial processes located onsite).

As part of the INFLUX experiment, flask and continuous measurements are collected at 12 tower locations within and around the urban area (Table 1 and Figure 1). We utilize existing cell phone and communications towers, and the sampling altitudes are 39–136 m above ground level (agl), with most above 100 m agl. Seven tower locations ring the outskirts of the urban area, four more towers are closer to the city center, and one tower is further downwind in the prevailing wind direction. Continuous measurements of CO$_2$ are made at all 12 towers, and continuous methane (CH$_4$) and CO measurements are made at a subset of the towers, all utilizing cavity ring-down spectrometers (CRDS, Picarro Inc.) [Crosson, 2008; Richardson et al., 2012]. Towers 1 and 2 have been operational since late 2010, with the remaining towers that also collect flask samples instrumented since mid-2012.

Flask samples have been collected from Towers 1 and 2 since December 2010, and at Towers 3, 5, and 9 since mid-2012 (Table 1 and Figure 1). These five towers all have both CO$_2$ and CO continuous CRDS measurements. A sixth roving flask sampler moves from tower to tower, both to provide comparisons between sites and methods, and to augment the flask measurements. The roving sampler has thus far provided samples from Towers 10 and 11, each for a period of a few months; neither of these towers currently
have continuous CO measurement. Flasks are filled by flowing air through a large-mixing volume over a 1 h period and then filling two flasks simultaneously from that mixing volume, providing a 1 h integrated air sample [Turnbull et al., 2012]. This sampling method integrates across a range of atmospheric turbulence and corresponding mole fraction variability that can otherwise complicate the interpretation of flask samples and the comparison with continuous data. It also allows for more direct comparison with mesoscale model results, which do not simulate turbulent fluctuations in atmospheric mole fractions. Most samples were collected over the hour starting at 2 P.M. local standard time (LST), but some samples early in the campaign were collected starting at 12 P.M. LST, and the last few samples were collected starting at 1 P.M. LST.

For each sample, two flasks are collected simultaneously. The flasks are each ~700 cc volume, are pressurized to ~2.5 atm when filled, and are housed in NOAA/ESRL Programmable Flask Packages (C. Sweeney et al., Seasonal climatology of CO2 across North America from aircraft measurements in the NOAA/ESRL Global Greenhouse Gas Reference Network, in review to Journal of Geophysical Research, 2015; http://www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html). One flask is analyzed for 50 species at NOAA/ESRL, including CO2, CH4, CO [Conway et al., 2012], and a suite of hydrocarbons and halocarbons [Montzka et al., 1993], and at University of Colorado Institute of Arctic and Alpine Research (INSTAAR) for stable isotopes of CO2 and CH4 [Vaughn et al., 2004]. The second flask is analyzed for the radiocarbon content of CO2 (14CO2) from which CO2ff is determined. Details of the 14CO2 analysis are given in section 2.3. When 14CO2 analysis is not required, both flasks have been measured for all the other species, providing a confirmation that both flasks represent the same air [Turnbull et al., 2012]. Flask CO2, CO, and CH4 have also been compared with the continuous CRDS measurements made at the same towers and averaged over the hour of flask sampling, and show excellent agreement in most time periods. The continuous CRDS-flask CO2 difference was shown to be 0.04 ± 0.38 ppm [Turnbull et al., 2012], for CO the CRDS is 3 ± 6 ppb lower than the flask measurements, and for CH4 the continuous CRDS measurements are 1 ± 5 ppb higher (Richardson et al., in preparation, 2015). A problem was identified with continuous CRDS CO measurements from Tower 2 during mid-2012, initially diagnosed from offsets between flask and continuous CRDS measurements. These have been flagged and removed from our analysis.

Flasks are filled in midafternoon when the boundary layer is likely to be mixed by convective turbulence and most easily modeled [Bakwin et al., 1998; Yi et al., 2001; Stull, 1988]. Figure 1 shows aggregated surface influence functions or footprints for midafternoon at Towers 1, 2, 3, 5, and 9, modeled using the Weather Research Forecast-Four Dimensional Data Assimilation model (WRF-FDDA) [Lauvaux et al., 2012] coupled to the Lagrangian Particle Dispersion Model (LPDM) [Uliasz, 1994] at 1 km resolution. The tower footprints were computed using the mean horizontal and vertical wind fields and the Turbulent Kinetic Energy field from the WRF-FDDA modeling system, coupled to the LPDM every 20 min. About 6500 particles were released every hour at the corresponding sampling heights to represent the hourly atmospheric concentrations.

Conditional sampling is used to restrict flask sample collection to days when the wind comes approximately from the western sector (ranging from northwest to southwest) such that Tower 1 provides an upwind background constraint. Under these sampling conditions, Tower 2 is immediately downwind of the urban area and measures components of the urban outflow, and Tower 9 is 24 km further downwind from Tower 2.

<table>
<thead>
<tr>
<th>Table 1. INFLUX Tower Sampling Information</th>
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<tr>
<td>Site</td>
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<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>Tower 1 Mooresville</td>
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<tr>
<td>Tower 2 E. 21st Street</td>
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<tr>
<td>Tower 3 Downtown</td>
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<tr>
<td>Tower 4 Greenwood</td>
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<tr>
<td>Tower 5 W. 79th Street</td>
</tr>
<tr>
<td>Tower 6 Lambert</td>
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<tr>
<td>Tower 8 Noblesville</td>
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<td>Tower 9 Greenfield</td>
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<td>Tower 10 Garfield Park</td>
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<tr>
<td>Tower 11 Butler University</td>
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<td>Tower 12</td>
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<td>Tower 13 Pleasant View</td>
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Under northwesterly or southwesterly conditions, Tower 9 does not sample the urban area. Tower 3 is situated in the heart of the urban area, approximately in line between Towers 1 and 2. Tower 3 is lower (54 m agl) than the other towers, and thus has a much stronger sensitivity to very local emissions than the other towers (Figure 1). Tower 5 is located in a suburban area to the north and is downwind of part of the urban area under southwesterly winds, but under more northwesterly conditions does not sample much of the urban plume.

As an exception, two samples were collected when the wind direction was from the east (4 and 5 November 2011), so that Tower 2 is the upwind constraint and Tower 1 is the downwind site. Therefore, we use Tower 2 for background and Tower 1 as the observation site for these two sampling dates to allow them to be directly compared with the remaining results. Here we focus on only three of the 50 trace gases measured, specifically

1. CO_{ff}, which is derived from $^{14}$CO_{2} measurements.
2. Total CO_{2}, which has both CO_{ff} and CO_{bio} sources (and/or sinks). From our atmospheric perspective, the CO_{bio} source is positive for respiration and biomass or biofuel combustion, and negative for photosynthetic uptake. We are primarily interested in the CO_{ff} source, but the CO_{bio} source makes CO_{2} a special case when examining the results, and we therefore discuss CO_{2} separately from the other species.
3. CO, which is produced during combustion, both from fossil fuel and biomass/biofuel combustion. The amount produced depends on the fuel carbon content and combustion conditions. CO is also produced by oxidation of biogenic VOCs with a maximum in summer. CO is consumed in the atmosphere by reaction with OH, with a lifetime of a few weeks to several months [Parish et al., 1993]. Finally, there is a small sink of CO to soils [Inman et al., 1971].

### 2.2. Lagrangian Framework and Urban Enhancements in Trace Gases

Urban trace gas emissions are always superimposed on a background mole fraction, which varies in time and space. Commonly, a Lagrangian framework is used to identify and remove the background signal and reveal the urban enhancements [e.g., Mays et al., 2009; Turnbull et al., 2011a]. In a simple Lagrangian air parcel framework, a parcel of background air with a background trace gas mole fraction is advected over the urban area, where trace gases are emitted and added to the air parcel. The same air parcel, observed downwind of the urban area, now has enhanced trace gas mole fractions. If the same air parcel is measured both upwind and downwind of the urban area and no mixing of that parcel with the surrounding atmosphere takes place, then the added trace gases can be quantified as the difference between the two, such that

$$\delta X = X_{\text{obs}} - X_{\text{bg}}$$  (1)

where $X$ is the mole fraction of the trace gas of interest (here total CO_{2} or CO), and the subscripts obs and bg indicate the observed (downwind) and background (upwind) mole fractions, respectively. Note that we denote the enhancement as $\delta X$ rather than $\Delta X$ to avoid confusion with $\Delta^{14}$C, the $^{14}$C content of CO_{2}.

This simplest possible, parcel-following Lagrangian framework assumes that the air parcel is altered only by emissions of trace gases from the urban area and that there are no other transport processes acting on the air mass to change mole fraction, such as entrainment of free tropospheric air or lateral mixing from air masses with different mole fractions. In practice, (a) it is impossible to identify and measure a single air parcel as it moves across an urban area, and (b) mixing/entrainment will always occur, in varying degrees depending on atmospheric conditions.

To address (a), if the background mole fraction is constant over some time period and/or spatial range, then the measurement of $X_{\text{bg}}$ is greatly simplified. In our tower experiment, we choose to approximate $X_{\text{bg}}$ by collecting and measuring samples obtained from Tower 1 at the same time as the downwind tower “observed” samples. Ideally, $X_{\text{bg}}$ would have been measured at Tower 1 at an earlier time, when the air parcel observed at each downwind tower was passing over Tower 1; for typical wind speeds of 2–5 m/s, Tower 1 sampling would be 2–6 h earlier than at the downwind towers. Thus, our use of simultaneous sampling effectively assumes that $X_{\text{bg}}$ has not changed for 2–6 h. We also assume that $X_{\text{bg}}$ is constant across a ~40 km distance, so that Tower 1 is representative of the upwind background constraint for the downwind towers for any wind direction ranging from SW to NW. Finally, we assume that vertical mixing (e.g., convective boundary layer entrainment) has not changed the mole fraction in the air parcel during advection from the background site to the observation site. This is valid if the difference between boundary layer and free tropospheric mole fraction is small, or relatively little entrainment takes place during the advection time.
These assumptions are highly idealized but enable a relatively straightforward evaluation of the flask observations. We will use this simple framework to examine what can be learned about urban emissions using this simplified model and will note when more complex descriptions of atmospheric transport and mixing are needed.

2.3. Determination of $\delta$CO$_2$ff From $^{14}$CO$_2$

Using our simple parcel-following Lagrangian framework, the recently added CO$_2$ff mole fraction ($\delta$CO$_2$ff) can be determined from $^{14}$CO$_2$ observations. The $^{14}$C content of CO$_2$ is reported as $\Delta^{14}$C, the permil deviation of the $^{14}$C content from that of a standard material, corrected for isotopic fractionation and radioactive decay since the time of collection [Stuiver and Polach, 1977]. $\delta$CO$_2$ff is determined from the observed ($\Delta_{obs}$) and background ($\Delta_{bg}$) $\Delta^{14}$C values and the observed CO$_2$ mole fraction (CO$_2$obs) [Levin et al., 2003; Turnbull et al., 2009].

$$
\delta\text{CO}_2\text{ff} = \frac{\text{CO}_2\text{obs}(\Delta_{obs} - \Delta_{bg}) - \text{CO}_2\text{other}(\Delta_{other} - \Delta_{bg})}{(\Delta_{ff} - \Delta_{bg})}
$$

(2)

$\Delta_{ff}$ is the $\Delta^{14}$C value of fossil fuel CO$_2$ (by definition $-1000\%$, the $\Delta^{14}$C value for zero $^{14}$C content). The second term of equation (2) is a small correction for other small sources of $^{14}$C primarily from heterotrophic respiration, and the nuclear industry and typical values are 0.2–0.5 ppm when a continental background is used [Turnbull et al., 2006, 2009; Miller et al., 2012], although it can be up to several ppm in locations close to nuclear industry sources [Graven and Gruber, 2011]. Although these other CO$_2$ sources may contribute in an urban setting, especially in summer, we will show that when a local background is used, these other CO$_2$ sources are small for our samples in winter. We set the second term of the equation to zero for all our measurements, noting that this may not be appropriate in summer (see section 3.2.2). Further, if the second term is constant across all samples in the data set, neglecting it does not change emission ratios calculated by the slope method (section 3.2).

The $^{14}$CO$_2$ sample preparation and measurement will be discussed in detail by J. C. Turnbull et al. (High-precision atmospheric $^{14}$CO$_2$ measurement at the Rafter Radiocarbon Laboratory, submitted to Radiocarbon, 2014). Briefly, CO$_2$ is cryogenically extracted from the flask samples at the University of Colorado INSTAAR. The CO$_2$ is either reduced to graphite at INSTAAR and measured by accelerator mass spectrometry (AMS) at the University of California, Irvine, or graphitized and measured by AMS at GNS Science, New Zealand. Replicate aliquots of CO$_2$ from air standard materials are used to determine the overall measurement precision. We determine two uncertainty values for each measurement. First, we determine the within-wheel reproducibility for air standard materials measured within each single AMS measurement wheel (measurement run). This within-wheel reproducibility is consistent with the counting statistical uncertainty and is typically 1.3‰ in $\Delta^{14}$C. When both $\Delta_{obs}$ and $\Delta_{bg}$ are determined from samples within the same wheel, as is the case for most INFLUX samples, this reproducibility is used in determining the CO$_2$ff uncertainty. The long-term repeatability of the same air standards across multiple wheels is slightly poorer than the within-wheel reproducibility, apparently primarily due to long-term variability in primary standardization. Thus, we determine an additional error term of 1.2‰ from the long-term repeatability and add it in quadrature to the counting statistical uncertainty in $\Delta_{obs}$ and $\Delta_{bg}$ when they are measured in separate wheels. For measurements made at INSTAAR/Irvine, only the long-term repeatability is reported [Lehman et al., 2013], and those values are used to determine $\delta$CO$_2$ff and its uncertainty. There appears to be a ∼1‰ offset between measurements at the two different AMS laboratories, which is ignored here since the $\Delta_{obs}$ and $\Delta_{bg}$ pairs are always measured at the same laboratory.

2.4. Continental Background Measurements of $^{14}$CO$_2$

A critical goal for INFLUX is to identify the optimal choice of background measurement location. For lack of a better option, many studies have chosen to use free troposphere or continental background sites to understand the impact of regional emissions.

The $^{14}$CO$_2$ record from Niwot Ridge, Colorado (NWR, 40.05°N; 105.60°W, 3739 m asl) [Lehman et al., 2013], along with other high-altitude mountain sites, has often been considered a good choice to characterize continental background $\Delta^{14}$CO$_2$ values [e.g., Levin et al., 2003; Hsueh et al., 2007]. NWR approximates $\Delta^{14}$CO$_2$ in the free troposphere over North America, and free tropospheric $\Delta^{14}$CO$_2$ measurements have also been used as a background constraint [Miller et al., 2012; Turnbull et al., 2011a]. However, being typically outside of the continental boundary layer, NWR will be affected by additional processes, possibly making it a poorer
background choice for some species than a continental boundary layer site [Turnbull et al., 2009]. Here we will examine the utility of this site as a background constraint for studying urban enhancements over Indianapolis. We follow previous practice for $^{14}$CO$_2$ measurement background, excluding NWR measurements that were possibly influenced by local emissions from the Denver metropolitan area, identified by CO mole fractions more than 15 ppb above the seasonal background value, and we apply a smooth curve to the remaining data [Turnbull et al., 2007].

Second, we consider $^{14}$CO$_2$ measurements from the WLEF television tower in Park Falls, Wisconsin (LEF, 45.95°N, 90.27°W, 470 m asl) as an example of a relatively clean surface continental site (LaFranchi et al., in preparation, 2015). LEF is located in a forested area, and samples are collected from 396 m above ground, consistently within the continental boundary layer during the daytime. Our INFLUX tower flask samples are only collected when the wind direction is from the west, so LEF is effectively upwind of our site, at a distance of about 900 km. LEF is influenced by CO$_2$ bio exchange and although the vegetation types in Indiana (agricultural) and at LEF (forested) are different, the general seasonal and diurnal cycles in CO$_2$ bio are expected to be similar. Therefore, we hypothesize that a smoothed curve of LEF $^{14}$CO$_2$ measurements might better approximate the continental boundary layer background than will measurements from NWR. We will demonstrate, however, that such a continental background site may not be sufficient for quantifying urban enhancements.

Figure 2. Trace gas measurements from the INFLUX towers. (a) The observed $^{14}$CO$_2$ at each tower, along with smoothed curve $^{14}$CO$_2$ values from NWR and LEF. (b) The calculated $\delta$CO$_2$ relative to Tower 1. (c) The observed CO$_2$ mole fractions. (d) CO$_2$ enhancements relative to Tower 1. (e) The observed CO mole fractions. (f) CO enhancements relative to Tower 1.
3. Results and Discussion

3.1. $\Delta^{14}$CO$_2$ and $\delta$CO$_2$ff

$\Delta^{14}$CO$_2$ is variable at all towers, ranging from $-21.6$ to $37.2$‰ (Figure 2). The highest $\Delta^{14}$C values show a downward trend consistent with NWR and LEF and a seasonal cycle consistent with that seen at the LEF surface site. Strong negative $\Delta^{14}$CO$_2$ deviations in many INFLUX tower samples are superimposed on this trend. $\Delta^{14}$CO$_2$ is consistently lower at the downwind towers than at the upwind Tower 1, which is remarkable considering the Tower 1 $\Delta^{14}$CO$_2$ values have considerable scatter through time. This suggests that, from the perspective of CO$_2$ff, Tower 1 is a good background site. Towers 2 and 3 show the largest negative deviations, whereas Tower 5 and Tower 9 are typically much more similar to Tower 1. This is consistent with emissions of $^{14}$C-free CO$_2$ff over the Indianapolis urban area, with the influence being most significant at the towers closest to the emission sources.

The Tower 1 $\Delta^{14}$CO$_2$ values are typically but not always substantially lower than both the free tropospheric background $\Delta^{14}$CO$_2$ at NWR and the presumed continental background at LEF during the same time period (Figure 2), indicating that Tower 1 is also influenced by some regional CO$_2$ff sources upwind of Indianapolis. This variability in $\Delta^{14}$CO$_2$ at Tower 1 is likely driven primarily by synoptic variability bringing air masses from different source regions and with different boundary layer residence times [e.g., Hurwitz et al., 2004]. For example, when the air mass comes from the northwest, it may bring pollution from the Chicago region to Tower 1, in varying mole fractions depending on the particular meteorological conditions and emission magnitude. The smoothed curves for NWR and LEF do not capture such synoptic features and instead reflect a generally “cleaner” signal with higher $\Delta^{14}$CO$_2$ values than those seen at Tower 1.

Calculated $\delta$CO$_2$ff at the downwind towers using Tower 1 background ($\delta$CO$_2$ff) ranges up to 10.8 ppm, with a median value of 1.1 ppm for all towers (Figure 2). One-sigma analytical uncertainties are typically 1.0 ppm but range from 0.6 to 1.7 ppm depending on the precision of the individual measurements. $\delta$CO$_2$ff varies on a synoptic scale, related to meteorological conditions and the extent of the urban footprint for each sample. For example, when the wind comes directly from the west, the footprint of a Tower 2 sample is dominated by the urban area, whereas when the wind is from SSW, the footprint contains a smaller portion of the urban area, likely resulting in lower $\delta$CO$_2$ff (Figure 1). Sampling dates with higher wind speeds and/or stronger vertical mixing can also be expected to result in lower observed $\delta$CO$_2$ff.

The median $\delta$CO$_2$ff values vary for each tower (Figure 3). Tower 3 typically has the highest $\delta$CO$_2$ff values with a median of 2.7 ppm. Tower 2 has median $\delta$CO$_2$ff of 1.5 ppm. Tower 5 occasionally has high $\delta$CO$_2$ff, but the median value is 0.5 ppm, and 60% of the Tower 5 $\delta$CO$_2$ff values are not significantly different (at one sigma) from zero. The median Tower 9 $\delta$CO$_2$ff is 0.1 ppm, indicating that on average Tower 9 is only very slightly...
enhanced in CO$_{2}ff$ relative to Tower 1. These patterns are consistent with the locations and footprints of the various towers (Figure 1). Tower 3 is the most “urban” tower, located in the central urban area, close to large traffic sources, and is also a relatively short tower, with the intake at 54 m agl. Tower 2 is on the edge of the urban area, further from the strongest emission sources than Tower 3. Tower 5 is in a suburban area northwest of the city center, upwind of part of the urban area under some flask-sampling conditions. Tower 9 is 24 km downwind of the urban area, so that when the wind is from NW or SW, it may not sample the urban plume, and, even when sampled, the emission plume will have been diluted by the time it reaches this tower.

The relatively large uncertainties in $\Delta^{14}$CO$_2$ measurements make detectability of $\delta$CO$_{2}ff$ using $^{14}$C an important consideration in choice of sampling location. $\delta$CO$_{2}ff$ is often indistinguishable from zero, even at the towers with the largest average signals. At Towers 2 and 3, 30% of our $\delta$CO$_{2}ff$ values are within one sigma of zero. There is no difference between summer and winter in the $\delta$CO$_{2}ff$ detectability. At Towers 5 and 9, where overall signals are smaller, 60% of $\delta$CO$_{2}ff$ values are indistinguishable from zero. This is despite our flask-sampling regime designed specifically to sample only when the towers are primarily downwind of the urban plume.

### 3.1.1. Effect of Choice of Background on $\delta$CO$_{2}ff$

Continental background sites such as NWR have often been used in determining $\delta$CO$_{2}ff$, so we test how using these backgrounds instead of our local upwind background Tower 1 would change our results. The mean $\delta$CO$_{2}ff$ from all the downwind towers using Tower 1 background is 1.1 ppm, whereas when NWR background is used, the mean $\delta$CO$_{2}ff$ is 3.4 ppm, 3 times higher. For individual samples, calculated $\delta$CO$_{2}ff$ can be up to 9.3 ppm higher when NWR is used as background. This suggests that when NWR background is used, $\delta$CO$_{2}ff$ represents CO$_{2}ff$ that has built up in the boundary layer and been advected to Indianapolis over the time.
scale of boundary layer to free troposphere mixing. When the NWR background is used, δCO$_2$ff therefore effectively represents CO$_2$ff emitted not only from Indianapolis but also from the broader continental region, including other urban areas and regional emission sources.

At LEF the Δ$^{14}$CO$_2$ signal has a more pronounced seasonal cycle than at NWR, with winter values ~5‰ lower than in summer (LaFranchi et al., in preparation, 2015). This may be due to the more stable winter boundary layer trapping of emitted CO$_2$ff in the region surrounding LEF [Turnbull et al., 2009]. In general, one might expect that the LEF site would be a more representative choice of background than NWR, as it should reflect similar boundary layer signals to Indianapolis, including the seasonal cycle in Δ$^{14}$CO$_2$ and in boundary layer stability. LEF does appear to be a better background choice than NWR, but δCO$_2$ff using LEF background still overestimates δCO$_2$ff, by a factor of about 1.9 compared to the local reference site.

Using the individual data rather than smoothed curves for NWR and LEF would not change the result in the case of the NWR measurements, which samples the free troposphere and is inherently less variable than sites within the boundary layer [Turnbull et al., 2007]. The LEF data do show some events with lower Δ$^{14}$CO$_2$ values, but these low Δ$^{14}$CO$_2$ events do not correlate well with the low Δ$^{14}$CO$_2$ events at Tower 1, and using the individual LEF data does not significantly change the interpretation.

Thus, we conclude that when the continental background values from LEF or NWR are used, the calculated δCO$_2$ff values at the downwind towers reflect CO$_2$ff from both Indianapolis and other regional sources. The location of Tower 1 just slightly upwind of Indianapolis (in our sampling conditions) suggests that it should result in δCO$_2$ff that approximates emissions from only Indianapolis. It is difficult to ascertain whether this is strictly true, and our simple Lagrangian parcel-following model does not account for all factors, particularly differential advection (i.e., heterogeneous boundary conditions and flow that is not directly from Tower 1 to the downwind towers). These issues notwithstanding, Tower 1 would appear to provide a more appropriate background for isolation of urban emissions coming primarily from Indianapolis, whereas using LEF or NWR as background appears to result in an overestimate of Indianapolis CO$_2$ff by a factor of 2 to 3.

### 3.2. Total CO$_2$

Total CO$_2$ is complicated by the CO$_2$bio source, which varies seasonally and diurnally in both magnitude and in sign. In winter, the two continental CO$_2$ sources, CO$_2$ff and CO$_2$bio (including respiration and biomass/biofuel burning), are both positive, causing higher CO$_2$ mole fractions at Northern Hemisphere sites. During daytime in summer, CO$_2$bio may be strongly negative, reflecting photosynthetic drawdown, but CO$_2$ff remains positive.

The observed baseline CO$_2$ mole fractions have a positive trend and strong seasonal cycle (Figure 2c), consistent with continental boundary layer CO$_2$ measurements [Andrews et al., 2014; Miles et al., 2012]. Yet large positive deviations from the baseline are apparent in all the INFLUX tower measurements. δCO$_2$ at the downwind towers relative to Tower 1 is consistently positive in winter (Figure 2c), and the summer δCO$_2$ values are also often positive and are even sometimes higher than those in winter. The positive enhancement is expected in winter, when both CO$_2$bio and CO$_2$ff are sources to the atmosphere. In summer, this is a somewhat surprising result, since summertime photosynthetic drawdown would reduce the magnitude, or even reverse the sign, of δCO$_2$. The median enhancement for each tower follows the same pattern as for


Table 2. Ratios R_{CO2} and R_{CO} for Various Data Sets

<table>
<thead>
<tr>
<th></th>
<th>Flask R_{CO2} δCO/δCO_{ff} (ppm/ppm)</th>
<th>Flask R_{CO} δCO/δCO_{ff} (ppb/ppm)</th>
<th>Flask R_{CO} δCO/δCO_{ff} (ppb/ppm)</th>
<th>In Situ All Hours R_{CO} δCO/δCO_{ff} (ppb/ppm)</th>
<th>In Situ 12–4 P.M. LST R_{CO} δCO/δCO_{ff} (ppb/ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tower 2 winter</td>
<td>79</td>
<td>1 ± 0.1 (0.8)</td>
<td>9 ± 2 (0.6)</td>
<td>9 ± 1 (0.8)</td>
<td>7 ± 1 (0.6)</td>
</tr>
<tr>
<td>Tower 3 winter</td>
<td>45</td>
<td>1.3 ± 0.1 (0.8)</td>
<td>7 ± 1 (0.7)</td>
<td>6 ± 1 (0.7)</td>
<td>6 ± 1 (0.8)</td>
</tr>
<tr>
<td>Tower 5 winter</td>
<td>44</td>
<td>1.1 ± 0.1 (0.8)</td>
<td>7 ± 1 (0.7)</td>
<td>6 ± 1 (0.7)</td>
<td>7 ± 1 (0.8)</td>
</tr>
<tr>
<td>Tower 9 winter</td>
<td>45</td>
<td>1.2 ± 0.1 (0.5)</td>
<td>9 ± 2 (0.5)</td>
<td>7 ± 1 (0.5)</td>
<td>7 ± 1 (0.7)</td>
</tr>
<tr>
<td>All towers winter</td>
<td>216</td>
<td>1.2 ± 0.1 (0.8)</td>
<td>8 ± 1 (0.7)</td>
<td>7 ± 1 (0.7)</td>
<td>7 ± 1 (0.6)</td>
</tr>
<tr>
<td>All towers all year</td>
<td>372</td>
<td>n/a</td>
<td>8 ± 1 (0.5)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Results are presented as the ratio ± uncertainty (r^2). Ratios are determined from the slope of the correlation between two species, using each data set as indicated. R_{CO2} is δCO versus δCO_{ff} from flasks. Flask R_{CO} from CO_{ff} is δCO versus δCO_{ff} from flasks. Flask R_{CO} from CO_{ff} is δCO versus δCO_{ff} from flasks. In situ 12–4 P.M. LST R_{CO} is δCO versus δCO_{ff} from the continuous CRDS measurements for 12–4 P.M. local standard time.

δCO_{ff}, with the downtown Tower 3 having the highest median value, followed by Tower 2 and Tower 5 (Figure 3). Median δCO2 at Tower 9 is somewhat higher than δCO_{ff}.

In order to better understand this δCO2 variability, we now examine the relationship between δCO2 and δCO_{ff} (Figures 4a and 5). We determine the ratio δCO2/δCO_{ff} (R_{CO2}) using the “slope method,” such that R_{CO2} is the best fit of a regression of δCO2 versus δCO_{ff}, using Type II regression which takes into account the errors in both quantities [Isobe et al., 1990]. Note that the uncertainty in the slope is determined from the regression, but it is known that for small data sets of fewer than 50 points the uncertainty from the regression can be strongly underestimated [Isobe et al., 1990]. As a secondary check on the slopes, we also used the “median method.” In this method, the ratio δCO2/δCO_{ff} for each individual sample is calculated, and R_{CO2} is determined as the median of all individual values [Miller et al., 2012]. In the median method, when δCO2 and/or δCO_{ff} are close to zero, the individual ratio can be wildly anomalous (whereas the slope method is much less sensitive to the outlier values). Thus, we propagate the uncertainty in the individual R_{CO2} and exclude those points where the uncertainty is greater than 2 ppm CO_{ff}/ppmCO_{ff} (which excludes those with enhancements close to zero, 25% of the original data points) before calculating the median value [Miller et al., 2012]. We found that in almost all cases, the median method gives results that overlap with the slope method result at one sigma; and therefore, we focus our discussion on the slope method results.

If δCO2 is entirely due to δCO_{ff}, then we would expect R_{CO2} to be unity. Yet gasoline in Indiana contains 8–10% bioethanol (U.S. Renewable Fuel Standard) [Energy Policy Act of 2005, 2005; Energy Independence and Security Act of 2007, 2007], and on-road mobile emissions comprise 37% of total CO_{ff} in Indianapolis [Gurney et al., 2012], so that bioethanol-derived CO_{ff} will be emitted at ~3% of the CO_{ff} emission rate. Human respiration also contributes CO_{ff} at 0.08 TgC yr^{-1} (assuming 93,000 gC yr^{-1} person^{-1} and a population of 900,000 for greater Indianapolis in 2011, www.statsindiana.edu), 2.5% of the CO_{ff} emission rate. Thus, if CO_{ff}, bioethanol, and respiration [Prairie and Duarte, 2007] were the only sources of CO_{ff} in the urban region, R_{CO2} = 1.05 would be expected. Higher values of R_{CO2} imply that additional CO_{ff} sources must contribute, and lower values imply a contribution from a CO_{ff} sink.

We calculate R_{CO2} on a month-by-month basis for Tower 2 and using all downwind towers using the slope method (Figure 5). Tower 2 monthly R_{CO2} includes data from 4 years (5–20 points for each month), whereas for the other towers, insufficient observations are available to calculate meaningful monthly R_{CO2} for the individual towers. The median method was not statistically different from the slope method, except during July to October, when the slope method has very large uncertainties (Figure 5). During the remainder of the year, R_{CO2} hovers around unity. For Tower 2, although not statistically different from 1.05, there does appear to be a bias to slightly lower values during the winter months, but this is not seen at the other towers. During the summer months of July–September, R_{CO2} is large and extremely variable. We divide the year into summer and winter, defining winter as the period when R_{CO2} is consistent, from November to April inclusive. Although October has R_{CO2} close to unity, there is considerable variability among the individual measurements, and we conservatively exclude these months from our “winter.” Next we pool all the winter months November to April inclusive into a single winter data set for further analysis. The summer results are discussed in section 3.2.2.

3.2.1. δCO2 in Winter

At Tower 2, δCO2 and δCO_{ff} correlate well (r^2 = 0.8) during winter (Figure 4a and Table 2). We find R_{CO2} of 1.0 ± 0.1 from the slope method and 0.9 from the median method (interquartile range 0.6–1.2). That is, R_{CO2} is not
significantly different from 1.05, the predicted value if $\delta$CO$_2$ is due to CO$_2$ff and associated bioethanol and urban human respiration. No terrestrial biosphere photosynthesis/respiration CO$_2$ sink/source is required to explain $\delta$CO$_2$. Winter $R$CO$_2$ at Towers 3 (1.3 ± 0.1), 5 (1.1 ± 0.1), and 9 (1.2 ± 0.1) are all slightly higher than $R$CO$_2$ at Tower 2, and using the median method gives statistically indistinguishable results. As we noted earlier, the uncertainties may be underestimated for small data sets, so the slightly higher values may be an artifact of only having 44 or 45 points in each fit (Table 2). We also considered whether the lower $R$CO$_2$ at Tower 2 compared to the other towers might be an effect of interannual variability, since the Tower 2 data set spans 2010–2014, whereas only 2012–2014 winter is used for the other towers. $R$CO$_2$ for Tower 2 for 2012–2014 winters was 1.1 ± 0.2, closer to the $R$CO$_2$ values for the other towers, but not significantly different from $R$CO$_2$ for the full Tower 2 measurement period, and still consistent with the predicted value of 1.05.

Thus, our results using Tower 1 as background imply that winter $\delta$CO$_2$ over Indianapolis is due almost entirely to CO$_2$ff, with a possible small contribution from bioethanol and human respiration emissions in winter, and no other significant sources, such as biomass combustion and biospheric respiration (CO$_2$bio), are apparent. The uncertainties on $R$CO$_2$ and the median $\delta$CO$_2$ff value mean that a small CO$_2$bio contribution of up to 0.3 ppm would not be detected in this analysis. Our result is contrary to previous studies that have found that when a regional or continental background is used, $R$CO$_2$ is about 2 [Levin et al., 2003; Turnbull et al., 2011b; Miller et al., 2012]. To examine this further, we calculate $R$CO$_2$ using the smoothed NWR and LEF background measurements of $\Delta^{13}$CO$_2$ and CO$_2$ (CO$_2$ smoothed curve data not shown). The apparent Tower 2 $R$CO$_2$ using LEF or NWR as background is 1.8 and 2.5 ppm/ppm, respectively. Both values are much higher than $R$CO$_2$ using Tower 1 as background of 1.0 ± 0.1 ppm/ppm. Thus, when LEF or NWR are used as background, only about half of $\delta$CO$_2$ at Tower 2 is explained by $\delta$CO$_2$ff, and the remainder must be due to respiration and/or biomass burning. This is consistent with a broader regional footprint at Tower 2 when LEF or NWR is used as background and is consistent with the previous studies that used free tropospheric or continental backgrounds [Turnbull et al., 2011b; Miller et al., 2012].

This result demonstrates that judicious choice of background measurements can isolate the urban flux of interest from the regional signal. Thus, for Indianapolis during wintertime, $\delta$CO$_2$ approximates $\delta$CO$_2$ff. Therefore, wintertime $\delta$CO$_2$ from continuous CRDS CO$_2$ measurements at the INFLUX towers can be used to obtain high temporal resolution $\delta$CO$_2$ff estimates (which may not be possible from sparse $^{14}$C measurements). This result is from a single urban area, and we caution that this may not apply to other locations, where source strength and seasonality in the CO$_2$bio flux may differ, and the relative magnitude of CO$_2$ff and CO$_2$bio fluxes will vary. This approach will only be valid when a local background that separates the urban emissions from those from the surrounding region is used.

### 3.2.2. $\delta$CO$_2$ in Summer

In summer, $\delta$CO$_2$ is often positive and often larger than $\delta$CO$_2$ in winter, an initially counterintuitive result. Our simple parcel-following Lagrangian framework assumes that the same air parcel was measured at Tower 1 and the downwind towers. Yet in this study, samples are collected at all towers simultaneously and we assume that the Tower 1 sample, while clearly not entirely the same air parcel as that measured at the downwind towers, is nonetheless representative of the background condition for the downwind towers.

Using the example of Tower 2, at typical wind speeds ranging from 2 to 5 m/s, an air parcel takes 2–6 h to move from Tower 1 to Tower 2, so that the Tower 1 background sample would more appropriately have been collected 2–6 h earlier than the Tower 2 sample. Yet boundary layer mixing has a strong diurnal cycle, resulting in large diurnal variability in the observed mole fractions of trace gases emitted at the surface even when the emissions are constant through time. Thus, sampling earlier in the day at Tower 1 could result in large biases in the calculated enhancements ($\delta$CO$_2$) simply because larger mole fractions would be observed earlier in the day when less vertical mixing occurs and emissions effectively build up in a shallower boundary layer. If boundary layer mixing follows the same diurnal pattern and magnitude at both Tower 1 and Tower 2 and the emission rate is constant, then this can be readily accounted for by sampling both towers at the same time.

In summer, the assumption of constant fluxes is violated, rendering the sampling of CO$_2$ at both towers at the same time a poor approach for using Tower 1 as a Lagrangian background site for Tower 2. Biospheric CO$_2$ emissions have a strong diurnal cycle in summer, due to the change from net emissions caused by nocturnal
CO radiotracers with the urban area. Median δCO at the INFLUX towers exhibits a seasonal cycle in the baseline values (Figure 2e), consistent with the seasonal cycle in background CO, which is mainly due to seasonality in the CO sink [Novelli et al., 1992]. Large positive CO excursions are superimposed on this background seasonal cycle, both at the upwind Tower 1 and the downwind towers. Nonetheless, the enhancement δCO at the downwind towers is almost always positive (Figure 2f). Our assumption is that regional CO sources can influence the Tower 1 CO mole fraction, and δCO at the downwind towers represents the CO added from the Indianapolis urban area. Median δCO at each downwind tower (Figure 3) follows the same pattern seen for δCO at the urban and regional scales [e.g., Bakwin et al., 1998; Davis et al., 2003] that accompany the diurnal cycle in summer.

Our choice of background can therefore result in an effective underestimate of the background CO mole fraction in summer and an overestimate in δCO. Our simple upwind-downwind sampling framework assumption is thus an invalid approximation for δCO in summer. A more sophisticated approach such as an atmospheric transport model is therefore needed to account for both the diurnally varying CO background and the varying vertical transport. In cases where high background variability occurs for other reasons, such as during frontal passage, this could also become important for other trace gas species.

3.3. Carbon Monoxide

The CO mole fraction at the INFLUX towers exhibits a seasonal cycle in the baseline values (Figure 2e), consistent with the seasonal cycle in background CO, which is mainly due to seasonality in the CO sink [Novelli et al., 1992]. Large positive CO excursions are superimposed on this background seasonal cycle, both at the upwind Tower 1 and the downwind towers. Nonetheless, the enhancement δCO at the downwind towers is almost always positive (Figure 2f). Our assumption is that regional CO sources can influence the Tower 1 CO mole fraction, and δCO at the downwind towers represents the CO added from the Indianapolis urban area. Median δCO at each downwind tower (Figure 3) follows the same pattern seen for δCO at the urban and regional scales [e.g., Bakwin et al., 1998; Davis et al., 2003] that accompany the diurnal cycle in summer.

In Figure 4 we plot δCO against δCOff, and the derived emission ratios (RCO) from the slope method are shown in Table 2. δCO and δCOff correlate reasonably well in winter (r² = 0.7) and slightly less well in summer (r² = 0.5). The winter correlations are not as strong as have been found in other studies, which have observed r² as high as 0.96 between CO and △13CO2-derived COff at the urban and regional scales [e.g., Turnbull et al., 2011a; Miller et al., 2012; Meijer et al., 1996; Vogel et al., 2010; Djurićin et al., 2010]. This is likely due to the mix of COff source types with varying CO contributions in Indianapolis, which may not be well mixed when sampling close to sources. Nonetheless, we observe a flask-based RCO of 8 ± 2 ppb/ppm for all flask measurements. This value is consistent in both summer and winter. There are small differences among the
towers (Table 2), but these are not statistically significant given the small data sets for Towers 3, 5, and 9. There is no apparent year-to-year trend in $\Delta$CO at Tower 2 over the four winters 2010–2014. Our flask-based $R_{CO}$ estimate is similar to but slightly lower than with other recent top-down observational studies in U.S. cities and regions (observations from 2004 to 2013), which have obtained $R_{CO}$ values ranging from 9 to 14 ppb/ppm [Turnbull et al., 2006; Graven et al., 2009; Wunch et al., 2009; Turnbull et al., 2011a; Miller et al., 2012; LaFranchi et al., 2013]. Our slightly lower values than observed previously are likely a consequence of two factors. The well-documented gradual decline in U.S. CO emission rates can be expected to result in slightly lower $R_{CO}$ for our 2010–2014 measurements than for the other studies with observations a few years earlier. A likely more important factor is the presence of the HSPP in central Indianapolis, contributing 29% of CO$_2$ff, but almost no CO. Most of the other observational studies were from western U.S. regions (Los Angeles, Sacramento, and Colorado) where large power generation facilities are located outside the respective urban areas, which would tend to drive up urban $R_{CO}$ relatively to our observations from Indianapolis. The Miller et al. [2012] study was over the broad northeastern U.S. region, and determined $R_{CO}$ of 10–13 ppb/ppm, not significantly higher than our result.

3.3.1. Winter $R_{CO}$ From Continuous CRDS CO and CO$_2$ Observations

We established in section 3.2 that $\Delta$CO$_2$ is a reasonable approximation for $\Delta$CO$_2$ff at our towers in winter. Therefore, we can use the ratio of $\delta$CO to $\Delta$CO$_2$ to approximate $R_{CO}$. Flask-based $R_{CO}$ from $\Delta$CO$_2$ff and $R_{CO}$ from $\Delta$CO$_2$ agree very well both for the total data set and for individual towers in winter (Table 2 and Figure 4).

There is good agreement between the flask and hourly average continuous CRDS CO$_2$ measurements (0.04 ± 0.38 ppm) [Turnbull et al., 2012]. The small offset in CO (3 ± 6 ppb) between the flask and continuous CRDS measurements (see section 2.1) will not change the results of $R_{CO}$ calculated from the slope method. On this basis, we consider the much larger data set of wintertime hourly averaged continuous CRDS CO and CO$_2$ measurements. A total of 14,468 winter hourly averaged observations are available. We determine $\delta$CO and $\delta$CO$_2$...
uncertainties in Hestia CO and (b) as we will show uncertainties in bottom-up CO emission estimates appear to be much larger than Wintertime continuous CRDS wind directions, was used.

mobile emissions sector CO emissions [e.g., construction equipment, lawnmowers, farm vehicles, and snowmobiles] account for another 24% or 79,000 tCO. According to the USEPA NEI2011, all other sectors, including industry, electricity generation, etc., are assigned as Other includes residential, industrial, commercial, and airport.

δCO₂ for the continuous CRDS measurements in the same manner as for the flasks, using the Tower 1 mole fractions for the same hour as the upwind background constraint. To provide a data set with comparable footprints to the flask measurements, we consider only the wintertime hourly averages when δCO₂ is positive, as an indicator that Tower 1 was upwind and provided a reasonable background constraint on these days. Continuous CRDS R_{CO} is then calculated from the correlation, using various subsets of the data (Table 2 and Figure 6). We also examined the influence of our choice of using only positive δCO₂ hourly averages and found that the slopes of the corrections were not significantly different when the full data set, including all wind directions, was used.

Wintertime continuous CRDS R_{CO} for the full diurnal cycle for all towers is 7 ± 1 ppb/ppm (r² = 0.8, Figure 7), agreeing very well with the flask-based R_{CO} values determined using CO₂ff and total CO₂. Using only midafternoon measurements from 12 to 4 P.M. local time (when flasks are collected) continuous CRDS R_{CO} is no different (Table 2). It is notable that the correlation is weaker (r² = 0.6) in the midafternoon than for the full diurnal cycle.

### 3.3.2. Winter R_{CO} Comparison With Bottom-Up Inventory-Based Estimates

Using R_{CO}, and assuming that the emission flux of CO₂ff is well constrained from the Hestia bottom-up data product, we can infer the CO emission flux [e.g., Turnbull et al., 2011a; Miller et al., 2012; LaFranchi et al., 2013]. This method relies on CO and CO₂ff being coemitted and requires an estimate of the spatial extent of the tower footprint. Although the footprints vary both between towers and day to day at individual towers, as R_{CO} is consistent across all four towers, we estimate that our continuous CRDS (midafternoon) R_{CO} of 8 ± 2 ppb/ppm is representative of the full urban footprint.

The Hestia bottom-up data product estimates the total CO₂ff emissions for Marion County in 2012 at 3.3 MtC yr⁻¹ [Gurney et al., 2012]. Using our R_{CO} value of 8 ± 2 ppb/ppm, we infer Marion County CO emission flux of 62,000 ± 16,000 metric tons (t) CO yr⁻¹. We assign the uncertainty based on the uncertainty in R_{CO} and do not consider uncertainty in the Hestia data product, as (a) the uncertainties in Hestia are not well quantified, and (b) as we will show uncertainties in bottom-up CO emission estimates appear to be much larger than uncertainties in Hestia CO₂ff emissions. We use Hestia 2012 CO₂ff estimates, as it is the middle year of our observations (2010–2014), and Hestia CO₂ff emission estimates for 2010 to 2012 change by only 4%.

The U.S. Environmental Protection Agency (USEPA) National Emission Inventory for 2011 (NEI2011) CO emission inventory [U.S. Environmental Protection Agency, 2013] reports Marion County CO emissions for 2011 at 164,000 tCO (Table 3), a factor of 2.6 higher than our inferred top-down estimate. The trend in USEPA NEI CO estimates through time suggests a possible decrease in CO emissions of a few percent from 2011 to 2012 (although 2012 data are not available), insufficient to explain the difference. A similar apparent overestimate of the CO emission flux from U.S. cities in the USEPA CO inventories has been observed in a number of studies in several other U.S. regions [Turnbull et al., 2006; Graven et al., 2009; Miller et al., 2012; Parrish, 2006; Hudman et al., 2008; Brioude et al., 2011; Kim et al., 2013] and is suspected to be due primarily to an overestimate of the on-road mobile emissions sector CO emissions [LaFranchi et al., 2013; Kota et al., 2014]. The USEPA NEI2011 also provides a breakdown of CO emissions by source sector, reporting that on-road vehicle (gasoline and diesel) emissions account for 69% of Marion County CO emissions or 114,000 tCO yr⁻¹ (Table 3). Off-road vehicles (e.g., construction equipment, lawn mowers, farm vehicles, and snowmobiles) account for another 24% or 40,000 tCO. According to the USEPA NEI2011, all other sectors, including industry, electricity generation,
waste disposal, biomass burning, and biogenic production of CO from vegetation and soils, contribute only 7% or 11,000 tCO. Thus, the NEI2011 overestimate of 102,000 ± 16,000 tCO relative to our top-down observation must be due primarily to the on-road and/or off-road vehicle sectors.

Bishop and Stedman [2008, hereinafter BS2008] directly measured on-road vehicle emission ratios from tail-pipe measurements in a number of U.S. cities, from which we derive an on-road vehicle \( R_{CO} \) estimate of 10–18 ppb/ppm in 2004–2007. McDaniell et al. [2013] combine BS2008 and other data to extrapolate on-road vehicle \( R_{CO} \) of 10–20 ppb/ppm for 2010. Using the Hestia \( R_{CO} \) estimate for Marion County, this range translates to 25,000–51,000 tCO yr\(^{-1}\) from on-road vehicles, much lower than the NEI2011 estimate for on-road CO emissions of 114,000 tCO yr\(^{-1}\). However, this revised estimate of on-road vehicle CO emissions is not sufficient to fully explain the difference between the USEPA bottom-up CO estimate and our top-down observations.

There is some evidence that off-road vehicle (including construction vehicles, farm vehicles, and snowmobiles) CO emissions may also be substantially overestimated in the USEPA NEI [Frey et al., 2008; Reid et al., 2010], but no improved estimates are available. Therefore, we make a simple assumption that the USEPA NEI2011 overestimates both on-road and off-road mobile emissions by the same factor, and scale the USEPA NEI2011 off-road mobile CO emissions down to 9000–18,000 tCO yr\(^{-1}\). We recognize that until additional data on off-road CO emissions are available, this is a significant source of error in our analysis. This gives a revised bottom-up estimate of 44,000–79,000 tCO yr\(^{-1}\), consistent with our observed value of 62,000 ± 16,000 tCO yr\(^{-1}\). In this revised bottom-up CO emission estimate, mobile emissions are still the dominant source of CO in Indianapolis, with relative contributions of on-road and off-road mobile sources of 56–64% and 20–22%, respectively. The revised inventory-based \( R_{CO} \) across all source sectors is 6–10 ppb/ppm.

This revision to the bottom-up inventory is also supported by the individual observed \( R_{CO} \) values. The USEPA NEI2011 inventory predicts \( R_{CO} \) for on-road and off-road mobile sources of 45 and 130 ppb/ppm, respectively. If this was the case, we would expect to observe occasional \( R_{CO} \) values that are close to these values. Yet the individual \( R_{CO} \) values never reach such high values, and instead fall within a range of about 0 to 25 ppb/ppm (Figure 4b).  

### 3.3.3. Winter Diurnal Cycles in \( \delta CO \), \( \delta CO_2 \), and \( R_{CO} \)

Now we use the large continuous CRDS CO and \( CO_2 \) data set to examine the diurnal variability of wintertime \( \delta CO \), \( \delta CO_2 \), and \( R_{CO} \). We separate the wintertime continuous CRDS hourly averaged observations by hour of the day and by tower. We further separate into weekdays and weekends, assigning weekends to span the hours from 7 P.M. LST on Friday evening until 7 P.M. LST on Sunday evening. We use the hourly average continuous \( CO_2 \) and CO values to calculate \( \delta CO_2 \) and \( \delta CO \) for each hour of each day at each tower. Next we construct the mean diurnal cycle in \( \delta CO_2 \) and \( \delta CO \) for weekdays and weekends separately. For each tower, 71–169 individual winter days are included in constructing the weekday diurnal cycle and 28–68 winter days are used to construct the weekend diurnal cycle. The number of days averaged varies depending on the number of hourly average continuous CRDS measurements available for that tower/hour.

We next determine the mean hourly \( CO_2 \) emission rate for each source sector for the winter months from the Hestia bottom-up data product for 2012 for weekdays and weekends (Figures 7a and 7e) and then calculate the total \( CO_2 \) emission for each hour (Figures 7b and 7f). To obtain the hourly average CO emission flux, we convolve the Hestia hourly \( CO_2 \)ff average for each \( CO_2 \)ff source sector with our revised sector-specific \( R_{CO} \) (Table 3) to obtain the CO emissions from each source sector. We then sum the CO emissions from all sectors (Figures 7c and 7g). It is worth noting that some aspects of the Hestia 2012 diurnal cycle are somewhat surprising. For example, Hestia 2012 indicates that residential \( CO_2 \)ff emissions are quite low during the midday hours on both weekdays and weekends in winter, even though it might reasonably be expected that at least some home heating (using natural gas and fuel oil) would continue throughout the day, especially on weekends. Nonetheless, the diurnal cycle is constructed from the best available data [Gurney et al., 2012].

The mean wintertime observed diurnal cycles in \( \delta CO \) and \( \delta CO_2 \) for each tower are also shown in Figures 7b, 7c, 7f, and 7g. The mole fractions are highest throughout the day at Tower 3 in the central urban area. On weekdays, a strong morning rush hour peak occurs at the same time as the morning bottom-up emission flux peak. A second, weaker, afternoon peak is also apparent and coincident with the bottom-up emission flux.

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peak. Mean δCO and δCO₂ values are lower at Towers 2 and 5, but the morning rush hour peak is still strongly apparent and a small increase in both species is observed in the late afternoon at Tower 5. Tower 9, located well downwind of the urban area, consistently has the lowest enhancements, with the morning rush hour signal hardly distinguishable, likely because the emission plume is more dispersed at this location. At Towers 2, 5, and 9, the observed peaks occur 1 to 2 h later in the observations than in the bottom-up emission flux, generally consistent with the transit time of air from the central city to these downwind towers.

Hestia 2012 predicts lower emissions fluxes on weekends than on weekdays, and this is also seen in the observations. The weekend observations do not exhibit the morning rush hour peak that is in the weekend Hestia estimate, although an evening peak is apparent in the observations. Only a weak morning rush hour peak is apparent in the weekend observations, whereas a more significant morning peak is seen in the Hestia data product. The evening peak apparent in the weekend observations is much later than that in Hestia.

As might be expected, a relationship between the observed δCO and δCO₂ and the bottom-up emission fluxes is evident but not direct. In the nighttime and early morning, the stable, low boundary layer results in strong buildup of emitted trace gases, whereas during the daylight hours, enhanced vertical mixing dilutes the emission flux and results in lower δCO and δCO₂, despite emission rates that are similar to, or higher than, the morning emission rates. Continuous measurements of the boundary layer height have recently been added to the INFLUX suite of observations, which may allow future analysis to separate changes in flux from changes in vertical mixing.

For each hour of the day at each tower, we calculate RCO using the slope method; two examples are shown in Figure 8 and the results are shown in Figures 7d and 7h. Uncertainties for hourly RCO values are typically several ppb/ppm. This means that it is difficult to draw conclusions based on a single hour of continuous CRDS data; thus, we draw qualitative conclusions by examining the full diurnal pattern. Using the bottom-up hourly CO₂ff and CO emission flux estimates, we also calculate bottom-up expected RCO (black lines in Figures 7d and 7h). On weekdays, all four towers and the bottom-up RCO estimate follow a similar diurnal pattern, with the lowest values in the early hours of the morning, and increasing through the morning, a dip through the middle of the day and another increase in the afternoon. The early afternoon at Tower 3 is an obvious exception which we will discuss separately. The diurnal cycle is less apparent in the observations on weekends, likely due to two causes: fewer data points and lower δCO₂ and δCO values. Both of these factors will result in RCO values that are expected to be noisier; this is most apparent at Tower 9 and we have excluded weekend Tower 9 RCO from the plot since it fluctuates between 4 and 8 ppb/ppm from 1 h to the next. The overall diurnal pattern for both weekdays and weekends is driven by the diurnal pattern in on-road vehicle emissions (Figures 7a and 7e), from which most CO is produced.

As seen from the mole fraction changes in δCO and δCO₂, there appears to be a 1 to 2 h phase offset in maximum RCO between the (whole city) bottom-up and observed tower estimates, consistent with the typical transport time from the urban emission source region to the downwind towers. Alternatively, this could indicate that the maximum vehicle usage occurs later in the day than predicted by Hestia.

Figure 8. Example correlation plots for determining hourly RCO from continuous CRDS data from (a) Tower 2 and (b) Tower 3.
The bottom-up $R_{CO}$ estimates are based on CO and CO$_2$ff emissions for the entire urban area. In contrast, the footprint for each tower sample is some portion of the urban area, depending on the tower location and the meteorological conditions at the time of sampling. $R_{CO}$ at Tower 5 is higher in the afternoon and early evening than at the other towers, perhaps indicating a stronger contribution of on-road vehicle emissions in the footprint of this tower, located in a suburban area away from (low $R_{CO}$) industrial sources.

The strong dip in $R_{CO}$ at Tower 3 during the midafternoon (local time) may relate to the footprint of this tower. Tower 3 is located in the central urban area (Figures 1 and 2) and close to many sources. The example Tower 3 $\delta$CO-$\delta$CO$_2$ correlation plot (Figure 8) shows much more scatter in the individual values and a significant number of points with high $\delta$CO$_2$, but very low $\delta$CO values, resulting in a lower overall $R_{CO}$. Also, note that the intercept on the Tower 3 example does not pass through zero, a consequence of the regression attempting to fit scattered results. Tower 3 is short relative to the other towers, at 54 m agl. Mesoscale modeling results indicate that Tower 3 is more strongly influenced by very local sources than the other towers, particularly during midafternoon (Figure 1). Thus, during midafternoon, Tower 3 observations represent emissions from only a small part of the urban area close to the tower, which are apparently source sectors with low characteristic $R_{CO}$.

During the nighttime, the bottom-up $R_{CO}$ estimate is lower than any of the tower observations, during both weekdays and weekends. One possible explanation is that Hestia underestimates nighttime on-road vehicle emissions. Indianapolis is on main interstate trucking routes, and anecdotal evidence suggests that nighttime heavy-vehicle traffic could be much higher than is included in Hestia. An alternative explanation is that on-road vehicle $R_{CO}$ is higher at night than during the day, due to the increased proportion of heavy vehicles. We tested this by increasing the nighttime on-road vehicle $R_{CO}$ to 20 ppb/ppm (versus 15 ppb/ppm) in our bottom-up CO calculation, and this improved the agreement, but was still insufficient to match the observations. A third explanation is that Hestia nighttime emissions from the residential and electricity sectors are too high, driving down the overall bottom-up $R_{CO}$ values. It is not possible to determine which of these possibilities is most likely from the top-down observations alone. Rather, this top-down information is being used to further examine the assumptions and areas of uncertainty in the Hestia data product.

The overall agreement between observed and bottom-up $R_{CO}$ estimates suggests that our revised source sector $R_{CO}$ values are reasonable, and that the diurnal cycle in the Hestia CO$_2$ff data product is generally accurate, at least for the mobile source sector for which this method is most sensitive, with the exceptions of a 1 to 2 h shift in the morning peak in the observations relative to Hestia and at nighttime. There remains considerable uncertainty in the estimate of on-road and off-road vehicle $R_{CO}$, and this needs to be better constrained to be able to provide quantitative source sector emission estimates from this method. These results show clearly that emission ratios can be used to capture the diurnal variability in CO$_2$ff source sector emissions, even in the presence of substantial diurnal variation in atmospheric stability and mixing.

4. Conclusions

We used tower flask samples to examine how the choice of background and downwind sampling location can influence estimates of $\delta$CO$_2$, $\delta$CO$_{ff}$, and $\delta$CO in an urban region. We found that when a background location directly upwind of the urban area such as our Tower 1 is used, the local urban emissions can be isolated from other sources. When background emission rates for a trace gas are roughly constant through the diurnal cycle, simultaneous measurement at upwind and downwind sites allows calculation of the urban enhancement in the species of interest. This is the case for most anthropogenic species including CO$_2$ff, CO, and in winter, total CO$_2$. In summer, diurnal variability in the background biogenic emissions of CO$_2$ means that our simple upwind-downwind Lagrangian method will bias our estimate of urban total CO$_2$ emissions.

The choice of downwind location and sampling height is also important. We showed that when measurements are made too far downwind, both plume dispersion and the relatively small proportion of the time that the location samples the plume reduce the detectability of the urban signal. This is especially important for $\delta$CO$_2$ff, for which uncertainties are large relative to the size of the signals. We found that for Indianapolis, our Tower 9 site 24 km downwind was too far away to reliably detect the urban CO$_2$ff signal. Our Tower 2 site just on the edge of the urban area was able to detect the urban signal most of the time, although for CO$_2$ff, one third of the measurements were still indistinguishable from background. The better CO$_2$ff...
detectability closer to the urban area needs to be weighted against homogenization of the urban plume. At Tower 3, in the central urban area and our shortest flask-sampling tower, observed mole fractions are largest, but different source sectors appear to influence this tower at different times of day, which may make it challenging to understand the overall urban emissions from measurements at this site.

\( \text{CO}_2 \text{ff} \) detectability will vary depending on the particular urban area being examined. Some common considerations will be the density of urban emissions and terrain. For example, an urban region with larger total emissions may not have higher observed \( \text{CO}_2 \text{ff} \) mole fractions if the urban extent is large and emission density relatively low. Complex terrain may result in buildup of emissions, resulting in better \( \text{CO}_2 \text{ff} \) detectability but more difficult emissions quantification. Finally, \( ^{14} \text{C} \) measurement precision is a dominant factor in \( \text{CO}_2 \text{ff} \) detectability, and even small improvements in precision will be useful.

For Indianapolis in winter, total \( \text{CO}_2 \) enhancements relative to the local Tower 1 background are almost entirely due to \( \text{CO}_2 \text{ff} \), so that \( \text{CO}_2 \) enhancement can be used as a proxy for \( \text{CO}_2 \text{ff} \). In contrast, when a free tropospheric or continental clean air background site is used, \( \text{CO}_2 \text{ff} \) contributes only about half of the \( \text{CO}_2 \) enhancement downwind of Indianapolis. Thus, raw \( \text{CO}_2 \) enhancement will frequently not be a good proxy for \( \text{CO}_2 \text{ff} \) when a continental background is used. We caution that our \( \text{iCO}_2 \) results represent measurements from a single urban area, in a single environment. The region surrounding Indianapolis has a strong seasonal \( \text{CO}_2 \) bio cycle, with a dormant biosphere in winter and strong biospheric exchange in summer. Many urban areas in different climate regimes will exhibit different \( \text{CO}_2 \) bio seasonality. The urban density and urban ecology may also differ in other urban areas. It is possible and even likely that relationships between \( \text{CO}_2 \text{ff} \) and other species, particularly total \( \text{CO}_2 \), will differ in other urban environments.

We were able to use characteristic \( R_C \) values for each source sector to examine the diurnal variation in the contributions of the \( \text{CO}_2 \text{ff} \) source sectors to the total \( \text{CO}_2 \) emissions. Our observations indicate that the USEPA NEI 2011 \( \text{CO} \) emission inventory is implausibly large, and we created a revised \( \text{CO} \) emission inventory for Indianapolis, albeit with some remaining uncertainties. The use of \( R_C \) allows us to directly compare observations with the Hestia bottom-up inventory estimates throughout the diurnal cycle. This ratio method circumvents the well-known difficulties with modeling the nighttime boundary layer which have made it difficult to use nighttime atmospheric observations to constrain fluxes [e.g., Lauvaux et al., 2012]. The atmospheric observations generally support the Hestia diurnal cycle in emissions, particularly the on-road emissions, to which \( R_C \) is most sensitive, but indicate a nighttime mismatch between the top-down observations and the bottom-up Hestia data product. A key remaining uncertainty for this method is in the source sector \( R_C \) values used to determine the bottom-up ratios. It is also important to note that in this study, we compared the city-wide bottom-up \( R_C \) estimate with observations from individual towers. Future work will use an atmospheric transport model to identify the footprint areas for each tower sample, allowing an improved understanding of the spatial variability in the \( \text{CO}_2 \text{ff} \) sources and source sectors.

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