

RESEARCH ARTICLE

Carbon monoxide isotopic measurements in Indianapolis constrain urban source isotopic signatures and support mobile fossil fuel emissions as the dominant wintertime CO source

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We present measurements of CO mole fraction and CO stable isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in air during the winters of 2013–14 and 2014–15 at tall tower sampling sites in and around Indianapolis, USA. A tower located upwind of the city was used to quantitatively remove the background CO signal, allowing for the first unambiguous isotopic characterization of the urban CO source and yielding ^{13}C of $-27.7 \pm 0.5\%$ VPDB and ^{18}O of $17.7 \pm 1.1\%$ VSMOW for this source. We use the tower isotope measurements, results from a limited traffic study, as well as atmospheric reaction rates to examine contributions from different sources to the Indianapolis CO budget. Our results are consistent with earlier findings that traffic emissions are the dominant source, suggesting a contribution of 96% or more to the overall Indianapolis wintertime CO emissions. Our results are also consistent with the hypothesis that emissions from a small fraction of vehicles without functional catalytic systems dominate the Indianapolis CO budget.

Keywords: Carbon Monoxide; Isotopes; Urban

1. Introduction

Urban carbon monoxide (CO) is a regulated pollutant that impacts human health and influences atmospheric chemistry via its interaction with OH and its role in tropospheric ozone production. Urban emissions are also an important component of the global CO budget (Crutzen, 1973; Crutzen, 1979; Logan et al., 1981; Duncan et al., 2007). Within urban areas of the United States, CO emissions inventories may be inaccurate by as much as a factor of two (e.g. Turnbull et al., 2015; Parrish et al., 2006; Graven et al., 2009; LaFranchi et al., 2013; EPA NEI 2011). In addition to the atmospheric chemistry and health

impacts, CO has been explored as a tracer for fossil fuel derived CO_2 ($\text{CO}_{2\text{ff}}$) (Meijer et al., 1996; Levin and Karstens, 2007; Turnbull et al., 2006; Vogel et al., 2010; Turnbull et al., 2011; Turnbull et al., 2015). This method relies on an assumption that CO is produced entirely by combustion, which is not always true within urban regions (Turnbull et al., 2015). Turnbull et al. (2015) found that during winter at Indianapolis, using CO as a correlate tracer yielded $\text{CO}_{2\text{ff}}$ enhancements that were in good agreement with those from ^{14}C measurements. This suggested that during the winter at Indianapolis, non-fossil fuel sources of CO do not contribute significantly. In contrast, during the summer, there is weaker correlation between CO and ^{14}C -derived $\text{CO}_{2\text{ff}}$ suggesting another summertime source of CO in Indianapolis (Turnbull et al., 2015) and in other locations (Turnbull et al., 2006; Miller et al., 2012). Stable isotopic measurements of urban CO can help quantify individual CO sources and sinks and provide an improved understanding of seasonal changes in the urban CO budget (e.g. Stevens et al., 1972; Brenninkmeijer, 1993; Conny, 1998).

In order to quantify the sources and sinks of CO via isotopic analysis, the ^{13}C and ^{18}O isotopic signatures need to be known (Stevens et al., 1972; Brenninkmeijer, 1993; Rockmann and Brenninkmeijer, 1997; Brenninkmeijer et al., 1999) (**Table 1**). To date, CO

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Table 1: Isotopic sources and sinks of carbon monoxide^a. DOI: <https://doi.org/10.1525/elementa.136.t1>

Isotopic Sources and Sinks				
Source/Sink	$\delta^{13}\text{C}$ (VPDB)	Uncertainty	$\delta^{18}\text{O}$ (VSMOW)	Uncertainty
Global Sources				
Fossil Fuel Combustion	-27.5‰	≤1‰	23.5‰	≤1‰
Biomass Burning	-22.9‰	1–3‰	17.15‰	1–3‰
CH ₄ Oxidation	-52.6‰	1–3‰	0‰	>3‰
VOC Oxidation	-32‰	1–3‰	0‰	>3‰
CO Oxidation by OH Fractionation Factors	5	unknown	-10	unknown
Urban and Traffic Emission Isotopic Signatures				
Study	$\delta^{13}\text{C}$ (VPDB)	Uncertainty	$\delta^{18}\text{O}$ (VSMOW)	Uncertainty
Stevens et al., 1972 “Engine” Emissions (World Average)	-27.4‰	0.3‰	24.6‰	~0.3‰
Mak and Kra, 1999 Spring Urban Emissions (USA)	-25.9‰	0.1‰	23.6‰	0.5‰
Mak and Kra, 1999 Fall Urban Emissions (USA)	-30.3‰	0.1‰	17.4‰	0.5‰
Sakugawa and Kaplan, 1997 (USA)	-26.3‰	unknown	21.5‰	unknown
Kato et al., 1999 Fleet CO (Germany)	-28.8‰	0.4‰	20.7‰	0.5‰
Kato et al., 1999 Uncatalyzed Gasoline Exhaust CO (Germany)	-29.9‰	0.3‰	22.3‰	0.3‰
Kato et al., 1999 Diesel Exhaust CO (Germany)	-22.2‰	1.1‰	10.9‰	0.8‰
Tsunogai et al., 2003 Fleet CO (Japan)	-25.2‰	1.5‰	23.7‰	1.8‰
Tsunogai et al., 2003 Uncatalyzed Gasoline Exhaust CO (Japan)	-27.9‰	1.1‰	18.7‰	3.2‰
Tsunogai et al., 2003 Catalyzed Gasoline Exhaust CO (Japan)	-23.8‰	0.8‰	25.3‰	1‰
Tsunogai et al., 2003 Diesel Exhaust CO (Japan)	-19.5‰	0.7‰	15.1‰	1.0‰
Popa et al., 2014 Fleet CO (Switzerland)	-25.6‰	0.2‰	24.1‰	0.2‰
Indianapolis Winter Emissions (This work) (USA)	-27.7‰	0.5‰	17.7‰	1.1‰

^aAdapted from (Brenninkmeijer et al., 1999) and (Gros et al., 2002) showing the major types of CO sources and their respective isotopic values. Also shown are urban and traffic emissions results from sources cited, as well as the results from this study.

isotope measurements have mainly focused on the global or hemispheric-scale CO budget (e.g. Brenninkmeijer et al., 1999), though several studies of CO isotopes in urban environments are available. Stevens et al., (1972) presented the first CO isotopic study to look at urban regions, and suggested that urban CO was likely dominated by traffic emissions (Table 1). Sakugawa and Kaplan (1997) measured urban CO isotopes within the Los Angeles Basin; they found that urban CO was dominated by fossil fuel combustion, with an unknown secondary source near the center of the city. This second source caused their results to differ somewhat in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from Stevens et al. (1972) (Table 1). Mak and Kra (1999) measured CO isotopes in air samples downwind of the New York metropolitan area and reported seasonal isotopic values of New York urban CO. The span of their results generally encompasses values found in Stevens et al. (1972) and Sakugawa and Kaplan (1997). Further, they identified an early summer “burst” of CO that they attributed to an increase in fossil fuel emissions from the urban center. All of these studies pointed to fossil fuel combustion as the main source of CO from within the city, but conclusive evidence was lacking. Gros et al. (2002) used measurements of CO isotopic signatures downwind of an urban center in Germany to identify pollution events and their sources, but did not quantify a unique urban isotopic signature.

Other studies of urban emissions scaled down further to constrain individual sources such as traffic and single vehicles. Kato et al. (1999) measured vehicle exhausts of uncatalyzed gasoline and diesel vehicles (Table 1). For cold engines directly after start-up, they reported identical results for catalyzed and uncatalyzed gasoline vehicles. They did not report values for catalyzed engines that were hot due to low CO mole-fractions that prevented accurate isotopic measurements. In addition, Kato et al. (1999) measured ambient air from the top of a building in Mainz, Germany and estimated an aggregate fleet $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Table 1). Tsunogai et al. (2003) performed similar measurements on vehicle exhaust and traffic emissions in Sapporo, Japan. They reported values for uncatalyzed gasoline engines, diesel engines and catalyzed vehicle exhausts (Table 1). They also measured the aggregate fleet traffic emissions (Table 1). These studies generally agree with one another within uncertainties, and show isotopic differences in CO vehicle emissions based on the type of fuel used, as well as the presence or absence of an exhaust catalyst (Table 1). Saurer et al. (2009) attempted to use the traffic values estimated in Kato et al. (1999) to constrain urban wood burning emissions, but did not account for a decade of changes to both catalytic technology and fuel isotopic composition. Popa et al. (2014), provided more recent estimations of traffic-emitted CO stable isotopes in Switzerland. They were able

to neglect background CO by measuring air in a tunnel with very high CO enhancements, obtaining an estimate of the aggregate Swiss fleet (**Table 1**). Due to variations in regional CO emission controls as well as differences in fuel sources (both of which affect the isotopic signatures of the emitted CO), the results published by Popa et al. (2014) are representative of traffic in Switzerland and possibly the greater European region, but cannot be assumed to be representative of other regions.

Despite these studies, large uncertainties still exist in the urban CO isotopic budget (**Table 1** and references therein). In all of the prior urban studies, the measurements represent a mixture of CO from background air coming into the city and CO produced within the city. This leads to uncertainty in the estimated urban source signatures. While this has not been shown directly for CO isotopic measurements, it has been well documented in other studies. For example, studies of CO₂ isotopes show the isotopic signature of the background air may change through time (Miller and Tans, 2003; Turnbull et al., 2015). Turnbull et al. (2015) demonstrated that a background measurement is necessary to properly quantify the urban CO and CO₂ plumes, and that the choice of background location can introduce biases if not considered carefully. Therefore, in order to fully characterize the urban CO isotopic signal, the background and urban contributions must be separated (discussed in more detail below). In addition, many of the cited studies are relatively out of date due to the evolving nature of catalytic CO removal in combustion emission controls, changes to the vehicle fleet fuel mixtures, and associated potential changes to fuel isotopic composition (Popa et al., 2014).

CO isotopic signatures of US urban CO emissions have not been measured in the last decade, with Sakugawa and Kaplan (1997) and Mak and Kra (1999) being the most recent US urban studies. The temporal and spatial changes in CO isotopic source signatures necessitate that CO isotopes need to be measured regularly to accurately characterize the CO isotopic budget (Popa et al., 2014). We conducted our study at Indianapolis, IN, the site of the Indianapolis FLUX project (INFLUX). INFLUX is a collaborative project focused on urban greenhouse gas emissions and involves ten institutions around the globe (Turnbull et al., 2015; <http://sites.psu.edu/influx>). The goals of INFLUX are to evaluate measurement techniques for assessing greenhouse gas emissions within an urban environment, and constrain bottom-up emissions data, models, and top-down estimates from tower and aircraft measurements. With the INFLUX infrastructure, we are able to quantitatively separate background CO signals from urban emissions, providing the first unambiguous isotopic characterization of urban CO sources.

Based on the results of Turnbull et al. (2015), the dominant source of CO at Indianapolis in winter was hypothesized to be fossil fuel combustion, particularly from mobile emissions. That study used measurements of the urban CO enhancement (CO_{enh}) and ¹⁴C-derived CO_{2ff} to determine that while the EPA NEI 2011 likely overestimates total CO emissions at Indianapolis, mobile emissions still account for between 77% and 87% of

total urban CO_{enh}. However, this assessment of mobile emissions is based on re-evaluating the emission sectors found in the EPA NEI 2011 based on the measured CO:CO₂ emission ratios and using the Hestia model product CO₂ from the mobile sector (Gurney et al., 2012; Turnbull et al., 2015). This provides strong evidence that the mobile sector is indeed the largest component of the CO budget during winter, but is not conclusive. To further investigate the hypothesis that mobile emissions are the dominant winter source of CO, we measured stable isotopes of CO during two winters at three tall towers located around and within Indianapolis, and conducted a limited traffic study.

2. Field and laboratory methods

2.1 Indianapolis FLUX project and tall tower sampling

INFLUX has twelve tall towers around the urban area (**Figure 1**) instrumented with in situ CO₂ mole fraction measurements; five towers have in situ CH₄ and CO mole fraction measurements, though only 2 of the towers have all three species measured currently (**Figure 1**) (Miles et al., 2017). At six of the towers, discrete air samples are collected about six days per month in the early afternoon (19:00 UTC, 13:00 local) when Tower 1 provides an upwind constraint and winds are roughly from the west (Turnbull et al., 2012) (**Figure 1**). Samples are collected in the early afternoon when boundary layer mixing is strongest. These air samples are collected into NOAA Portable Flask Packages (PFPs). A full description of the PFP construction, and CO stability during storage can be found on the NOAA GMD website (<https://www.esrl.noaa.gov/gmd/ccgg/aircraft/sampling.html>). Briefly, the PFP's consist of 12 borosilicate glass containers that are cleaned and tested for stability of CO during both short (7 day) and long (1 month) term storage. CO mixing ratio has an approximate short term storage stability of 0.15 ± 1.4 ppb and a long term storage stability of 1.3 ± 2.7 ppb. An additional single test with a PFP filled with our standard gas that was left to sit for 5 days showed no statistically significant change in CO isotope values over this period.

A full description of the PFP sampling procedure at the INFLUX towers can be found in Turnbull et al. (2012). Briefly, samples are taken using a 15 L integrating volume, 2 compressors, and a flow meter, which allow for a 1-hour time-integrated sample (Turnbull et al., 2012). The samples are dried prior to entering the collection system. The advantage of this type of system is that changes in mole fraction of the various trace gasses on very short time scales do not bias the sample. CO stable isotopic measurements are made on PFPs from Towers 1 (121 m above ground level (AGL)), 2 (136 m AGL), and 3 (54 m AGL) (**Figure 1**) and for this study were taken during the months of November 2013–January 2014 and November 2014–February 2015 (inclusive). CO and CO₂ mole fractions used in this study were measured at NOAA ESRL (Novelli et al., 2003; Zhao and Tans, 2006) on the same PFPs that were used for CO stable isotope analyses.

Tower 1 is treated as a background site, and Towers 2 and 3 as sites affected by the urban CO source (**Figure 1**). Tower 1 measures rural air, with few population centers. Tower 2 is to the east of the city center and effectively

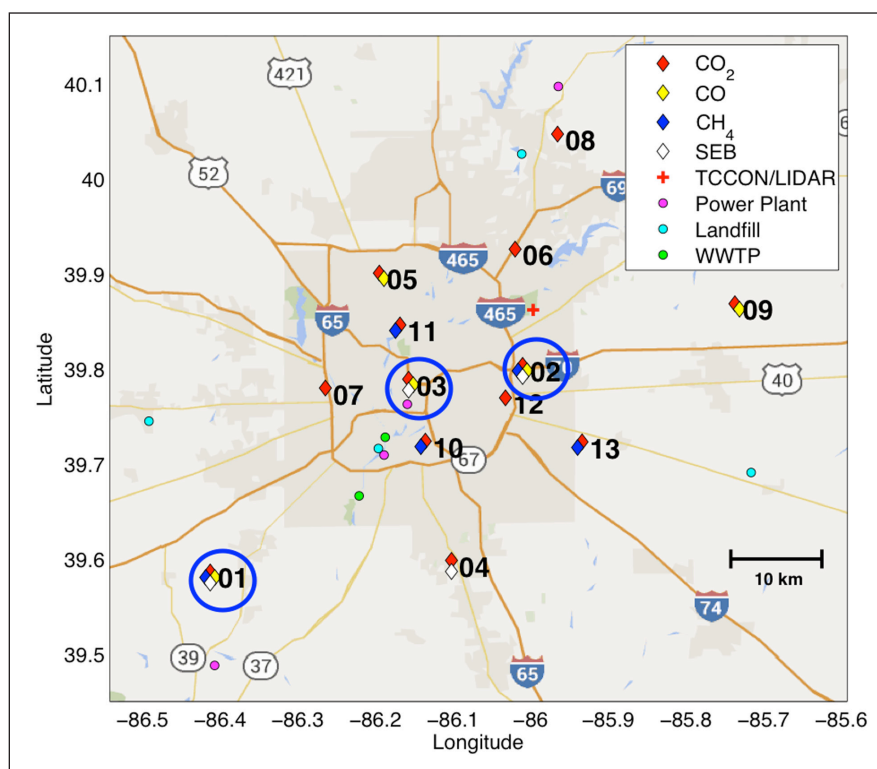


Figure 1: Map of the Indianapolis FLUX campaign. CO stable isotopes are measured in samples collected at tall towers at locations 1, 2, and 3. See supplemental material for wind directions during all measurements days and associated back-trajectories. (Miles et al., 2017). CO₂, CO, and CH₄ indicate locations of continuous CRDS measurements, SEB indicates a Surface Energy Balance experiment, TCCON/LIDAR indicate a site for lidar based Total Column Carbon Observing Network experiments, and WWTP sites are Waste Water Treatment Plants. DOI: <https://doi.org/10.1525/elementa.136.f1>

measures the entire urban pollution plume. Tower 3 is at the center of the “downtown” region of Indianapolis, and is affected by part of the urban CO emissions. As samples are only collected when winds are roughly from the west (180°–360°), CO, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ measured at Tower 1 provide a background for the measurements at Towers 2 and 3. Thus, the urban pollution signal can be unambiguously quantified. The distance separating Tower 1 and Tower 2 is 50.8 km and Tower 1 and Tower 3 is 36.2 km. The air mass transit time is variable but for the samples in this study, the overall average transit time for Towers 2 and 3 was ≈ 2.5 hours (~ 6 m/s mean wind speed) (supplemental material, Table S1).

2.2 CO Stable isotope measurements

A new analytical system for CO isotope analyses in small (≈ 80 cc at standard temperature and pressure (STP)) air samples was developed at the Institute of Arctic and Alpine Research (INSTAAR) at the University of Colorado (Boulder, CO, USA). This system and its development will be described in detail in a future publication. The system design generally follows the work of Mak and Yang (1998) but with some improvements that allow for negligible system blanks. The system’s long-term precision is 0.23‰ for $\delta^{13}\text{C}$ and 0.46‰ for $\delta^{18}\text{O}$ (1σ , 84 measurements in a known standard run as a sample over two years) (supplemental material, section 2). We note that all d values in this work are reported with respect to the international

standards Vienna P.D. Belemnite (VPDB) ($\delta^{13}\text{C}$) and Vienna Standard Mean Ocean Water (VSMOW) ($\delta^{18}\text{O}$).

The air samples are pulled by vacuum from the PFP flask through a first cryogenic trap (-70°C) to remove water vapor from the sample stream. A Mass Flow Controller (MKS π -MFC) regulates air flow at 20 cc/min (STP). Following the first cryogenic trap, the sample enters a borosilicate glass line where condensables (CO₂, N₂O, hydrocarbons, any residual H₂O vapor) are removed via another 8-loop cryogenic trap at -196°C . CO is then oxidized to CO₂ using Schütze’s reagent (I₂O₅ and H₂SO₄ on a silica gel matrix) (Smiley, 1949). After oxidation, the air first passes through another cryogenic trap at -70°C to remove any H₂SO₄ released from Schütze’s reagent; CO-derived CO₂ is then trapped cryogenically in a 4 loop trap at -196°C . Sample collection time (and therefore sample air volume) is adjusted so that each sample or standard aliquot yields ~ 11 ng of CO-derived carbon. This way, every measurement gives approximately the same response in the mass spectrometer, removing the need for linearity corrections. After collection of the sample, the extraction line is evacuated and an ultra-pure He carrier flow is started to transfer the sample to a cryofocusing trap. The cryofocus consists of a single loop of fused silica tubing immersed in liquid nitrogen. Following the cryofocusing step, the sample is carried by ultra-pure He to an IsoPrime IRMS via a GC column (used to shape the peak for optimal integration).

We analyze samples and two cylinders of clean ambient air that serve as standard gasses each day. One standard was filled at Niwot Ridge, Colorado by NOAA GMD, and the other at Baring Head, New Zealand, by the National Institute of Water and Atmospheric Research (NIWA), in Wellington, New Zealand. Both standards were isotopically calibrated by NIWA using a large-volume CO isotope extraction system (Brenninkmeijer, 1993). The Niwot Ridge standard is used to correct both the samples and the Baring Head standard to VPDB and VSMOW. The Niwot Ridge standard is run at the beginning and end of each sample set (three sample extractions and one Baring Head standard extraction). The amount of air made available for this study allows for only a single extraction for each sample. Because of this, the repeatability of CO isotopic values obtained for the Baring Head standard (0.23‰ for $\delta^{13}\text{C}$ and 0.46‰ for $\delta^{18}\text{O}$) is used as an estimate of sample uncertainty. The Baring Head standard is also used to monitor the short- and long-term repeatability of the extraction system.

$\delta^{13}\text{C}$ of the sample on the VPDB scale is calculated as follows:

$$\delta^{13}\text{C}_{\text{sa-VPDB}} = \left[\left(\frac{\delta^{13}\text{C}_{\text{sam:MSref}}}{1000} + 1 \right) \times \left(\frac{\delta^{13}\text{C}_{\text{Niwot:VPDB}}}{1000} + 1 \right) \right] \times 1000 \quad (1)$$

Where sam:MSref is the sample delta value with respect to the mass spectrometer reference gas (pure CO_2), Niwot:MSref is the Niwot standard gas delta value with respect to the mass spec reference gas, and Niwot:VPDB is the calibrated Niwot standard gas delta value with respect to VPDB.

$\delta^{18}\text{O}$ is calculated based on the following equation (Brenninkmeijer, 1993; Mak and Yang, 1998):

$$\delta^{18}\text{O}_{\text{CO}} = 2\delta^{18}\text{O}_{\text{CO}_2} - (2\delta^{18}\text{O}_{\text{CO}_2\text{std}} - \delta^{18}\text{O}_{\text{COstd}}) \quad (2)$$

where $\delta^{18}\text{O}_{\text{CO}}$ is the $\delta^{18}\text{O}$ of sample CO, $\delta^{18}\text{O}_{\text{CO}_2}$ is the $\delta^{18}\text{O}$ of CO_2 derived from sample CO after oxidation by the Schutze reagent, $\delta^{18}\text{O}_{\text{CO}_2\text{std}}$ is the $\delta^{18}\text{O}$ of CO_2 derived from Niwot Ridge standard CO after oxidation by the Schutze reagent, and $\delta^{18}\text{O}_{\text{COstd}}$ is the $\delta^{18}\text{O}$ of Niwot Ridge standard CO. All the $\delta^{18}\text{O}$ values are with respect to VSMOW. $\delta^{18}\text{O}_{\text{COstd}}$ on the VSMOW scale is known from calibration at NIWA as described above. $\delta^{18}\text{O}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{CO}_2\text{std}}$ on the VSMOW scale are determined using:

$$\delta^{18}\text{O}_{\text{CO}_2\text{-VSMOW}} = \left[\left(\frac{\delta^{18}\text{O}_{\text{sa-MSref}}}{1000} + 1 \right) \times \left(\frac{\delta^{18}\text{O}_{\text{MSref-VSMOW}}}{1000} + 1 \right) - 1 \right] \times 1000 \quad (3)$$

Where $\delta^{18}\text{O}_{\text{sa-MSref}}$ is the measured $\delta^{18}\text{O}$ of either sample or Niwot Ridge standard gas CO-derived CO_2 with respect to the pure CO_2 used as the mass spectrometer reference gas. $\delta^{18}\text{O}_{\text{MSref-VSMOW}}$ is the $\delta^{18}\text{O}$ on the VSMOW scale of the pure CO_2 used as the mass spectrometer reference gas; this was determined on a separate instrument located at INSTAAR

which routinely measures stable isotopes of CO_2 (Trolier et al., 1996).

Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are measured on the mass spectrometer as ratios of atomic masses of 45/44 and 46/44, respectively. However, since there are other isotopologues of CO such as C^{17}O , which has the same mass as ^{13}C , a correction must be applied to account for this difference. For this study, we use the algorithms detailed in Brand et al. (2009) for this correction.

2.3 Regression plot data analysis

In order to separate the isotopic source signature of the polluted air within the city from the background, we used a regression plot approach (Miller and Tans, 2003). Starting from two mass balance equations:

$$\text{CO}_{\text{obs}} = \text{CO}_{\text{bg}} + \text{CO}_s \quad (4)$$

$$\delta_{\text{obs}}\text{CO}_{\text{obs}} = \delta_{\text{bg}}\text{CO}_{\text{bg}} + \delta_s\text{CO}_s \quad (5)$$

where CO indicates the mole fraction, “ δ ” indicates either $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$, ‘obs’ indicates the measured value, ‘bg’ indicates an unpolluted background value, and ‘s’ indicates an added source which may be a mixture of multiple difference sources (Miller and Tans, 2003). Combining and solving (4) and (5) for δ_s yields:

$$\delta_s = \frac{\delta_{\text{obs}}\text{CO}_{\text{obs}} - \delta_{\text{bg}}\text{CO}_{\text{bg}}}{\text{CO}_{\text{obs}} - \text{CO}_{\text{bg}}} \quad (6)$$

Using an ordinary least squares (OLS) regression (Zobitz et al., 2006), the source delta value can be obtained by regressing the difference between the difference in the product of the mole fractions and the isotopic values against the background and observed mole fractions. In this case, the ‘obs’ value is one of the two polluted towers (Towers 2 or 3), and the ‘bg’ value is the background tower (Tower 1).

Each isotope and mole fraction measurement has associated measurement uncertainty; therefore, a Monte Carlo approach was used to determine the best-fit source value taking the measurement uncertainty into account. Each point is assigned a normal probability distribution with a mean equal to the measured value, and σ equal to the 1σ uncertainty on the measurements. We tested the assumption of normality by using a quantile-quantile plot of residuals from a single fit of the measured points from the towers. This test of our residuals indicates our error is not strictly normal, but that using a normal distribution for error approximation is still reasonable. Ten thousand OLS regressions were run with values randomly selected from each of the probability distributions and the slopes and r^2 values from each regression were recorded. This set of slopes was averaged, and the standard deviation on that set of slopes was taken. The δ_s values reported from this analysis are the mean value of each Monte Carlo simulation slope and the uncertainty reported is the 1σ uncertainty calculated from the set of slopes produced by the simulation. The r^2 values reported are the mean of the set of r^2 values from each simulation.

2.4 Traffic study

A limited traffic study was conducted on Thursday, March 5th and Friday, March 6th 2015. The goal of this study was to sample typical traffic CO emissions in Indianapolis, as well as emissions from several individual vehicles. Briefly, air was analyzed and sampled using a cavity ring down spectrometer (CRDS) 4-species analyzer (CO, CH₄, CO₂, H₂O) (Picarro Inc. CA, USA) in conjunction with a NOAA GMD Programmable Compressor Package (PCP) and PFPs (Sweeney et al., 2015). These instruments were installed in a vehicle and two sample inlets were run to the outside of the vehicle, and collocated to ensure they sampled the same air. Ten flask samples were collected and analyzed for CO mole fraction and CO stable isotopes. During flask sampling, the CRDS was used as a guide, indicating when the sample inlet was positioned in a vehicle plume. Three background samples were also taken to the west of the city (wind was coming from the west) in a nature preserve; sampling was done when the CRDS analyzer indicated clean air was entering the sample inlet. This site was chosen to measure background air because it was near the Tower 1 location, and had no major traffic sources nearby. For a detailed description of the traffic study measurements, see Table S3.

2.5 Simplification of the Indianapolis winter CO budget

The main sink of CO is oxidation by OH (Logan et al., 1981; Duncan et al., 2007). However, we are able to ignore the sink for the winter Indianapolis urban budget because of the short transit time between the background and polluted towers. We calculated the effect of CO oxidation by OH during the winter by determining its reaction rate ($k_{\text{OH,CO}}$) for a typical Indianapolis winter day. We used an [OH] of 2×10^6 molecules/cm³ (Atkinson et al., 2003), measured values of CO, typical atmospheric temperature and pressure for the region and parameters from Sander et al. (2006) to determine $k_{\text{OH,CO}}$. Given the average transit time of two hours between the towers, the total impact on CO mole fraction, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ from oxidation CO by OH was calculated to be a loss of 0.5 nmol* mol^{-1} CO, a change in $\delta^{13}\text{C}$ of $-1.5 \times 10^{-5}\text{‰}$, and a change in $\delta^{18}\text{O}$ of $3.2 \times 10^{-5}\text{‰}$; this change is insignificant relative to our measurement errors and can therefore be ignored (Table S2, supplemental material). For this budget simplification, we are using fractionation factors of 5‰ for $^{13}\text{C} + \text{OH}$ and -10‰ for $^{18}\text{O} + \text{OH}$ (Brennikmeijer et al., 1999) (Table 1, supplemental material section 3).

Methane and non-methane hydrocarbon (NMHC) oxidation accounts for approximately half of the global CO budget (Duncan et al., 2007) and we estimate the contribution of these to the wintertime Indianapolis urban CO budget. Compounds such as OH and O₃ readily oxidize CH₄ and many NMHCs (Sander et al., 2006; Warneke et al., 2013; Russo et al., 2011; Khan et al., 2015) making them seasonally-varying sources of CO (Duncan et al., 2007). However, the relatively low wintertime NMHC and OH mole fractions (Helmig et al., 2013; Hu et al., 2015) mean that CH₄ and NMHC oxidation may be unimportant for our study. Not all NMHC species capable of impacting CO are measured

at INX; therefore some of the NMHC mole fractions are estimated using other urban studies in the literature (Warneke et al., 2013; Russo et al., 2011; Khan et al., 2015) (Table S2, supplemental material). Reaction rates with OH were calculated using k_{OH} from Warneke et al. (2013) if available, and if not, k_{OH} was calculated using parameters from Sander et al. (2006), and Atkinson et al., (1999, 2003, 2006). Where applicable, k_{O_3} was also calculated using the parameters from Sander et al. (2006) and Atkinson et al. (1999, 2003, 2006). For CH₄ and all NMHC species combined, the estimated average effect on CO mole fraction and CO isotopes during air transit between Tower 1 and Tower 2 or 3 is $+2.3 \text{ nmol mol}^{-1}$, 0.10‰ for $\delta^{13}\text{C}$, and 0.36‰ for $\delta^{18}\text{O}$ (Table S2, supplemental material). This is below the estimated measurement uncertainty for our individual isotopic measurements.

Further, we note that our estimates of impacts of CH₄ and NMHC oxidation as well as CO removal by OH likely represent an upper limit. OH is photochemically produced in the atmosphere, and its mole-fraction is strongly dependent on insolation, with minimum OH mole fraction occurring in the winter (Logan et al., 1981). Our use of globally averaged OH mole fraction in the calculations therefore likely results in an overestimation of the reaction yields, and places upper bounds on the oxidation sources and sink (supplemental material).

Because these oxidation reactions can be neglected, the remaining sources of CO within the urban region are all combustion sources. They include biomass burning for residential heat, fossil fuel combustion by vehicles, residential and commercial heating, and power generation.

3. Results and discussion

3.1 Time-series record of CO and its stable isotopes

We analyzed approximately 18 samples per month (6 from each tower) from July of 2013–August of 2015 (Figure 2). This main focus of this study is on the simpler, wintertime budget, but we provide a brief overview of the entire data set here.

As expected and as previously observed (e.g. Novelli et al., 1998), CO mole fraction is strongly influenced by seasonal changes in OH, with CO increasing during the fall to a maximum in mid-winter, and decreasing to a minimum during the late summer (Figure 2). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ also show clear seasonal cycles (Figure 2). The seasonal cycles of CO mole fraction and $\delta^{13}\text{C}$ co-vary and lag behind $\delta^{18}\text{O}$. This result is similar to those found at another mid-latitude continental site, Mount Sonnblick in the Austrian Alps (47°N, 3106 m above sea level) (Gros et al., 2001). This pattern deviates from a typical high latitude background site, where $\delta^{13}\text{C}$ tends to lag behind both CO mole-fraction and $\delta^{18}\text{O}$ (Rockmann et al., 2002). Our results show significant scatter in CO mole fraction and $\delta^{18}\text{O}$ but less in $\delta^{13}\text{C}$ (Figure 2). Again, this result is similar to the Mount Sonnblick study (Gros et al., 2001) and differs from the high latitude background site (Rockmann et al., 2002). However, compared to the high latitude site (Rockmann et al., 2002), and the Mount Sonnblick site (Gros et al., 2001), the amplitude of the seasonal cycles in our study are muted.

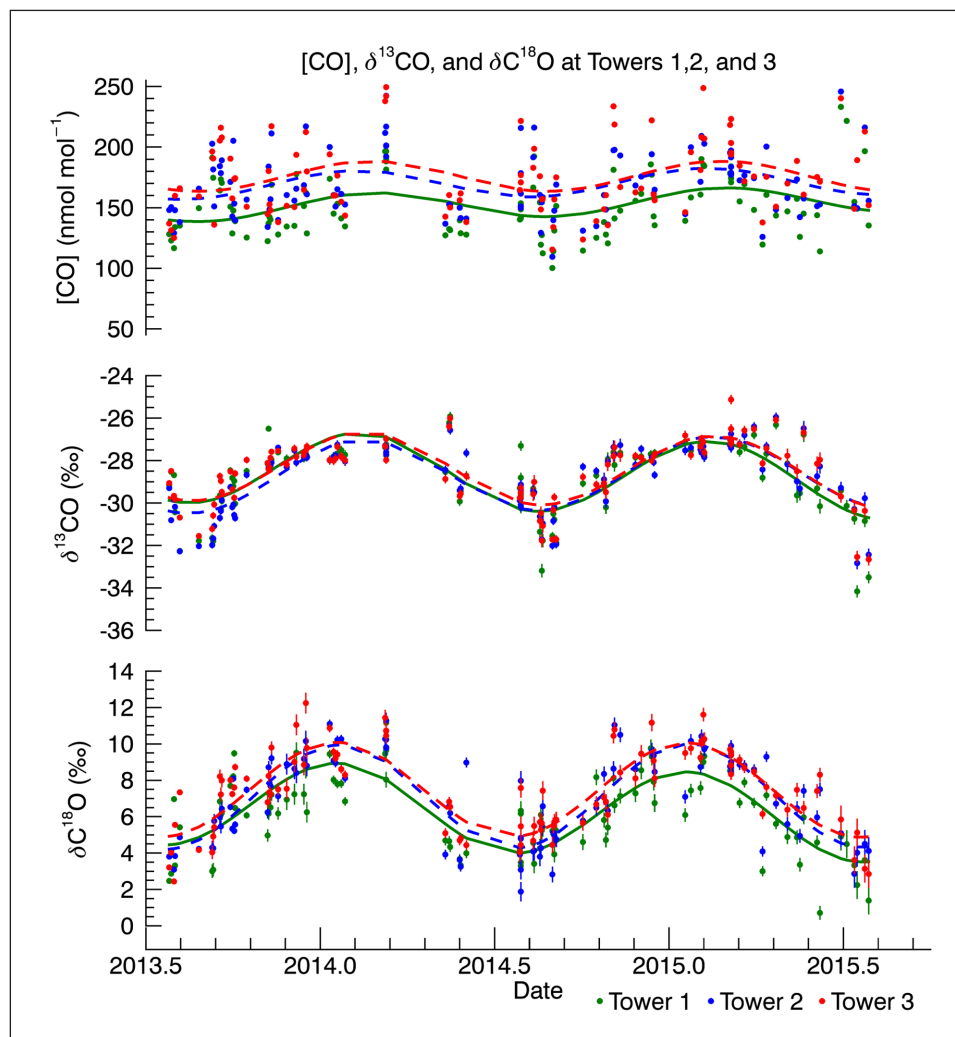


Figure 2: Time series of CO, $\delta^{13}\text{CO}$, and $\delta\text{C}^{18}\text{O}$ at Towers 1, 2, and 3. CO mole fraction (top), $\delta^{13}\text{CO}$ (middle), and $\delta\text{C}^{18}\text{O}$ (bottom) for Towers 1 (green), 2 (blue), and 3 (red) for the two years of the measurement campaign. Error bars are 1 sigma standard deviation of a standard gas which was run as a sample for each month of measurement. This standard is calibrated for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and thus provides a metric for the instrument precision and accuracy. DOI: <https://doi.org/10.1525/elementa.136.f2>

The difference between Indianapolis and these other sites is expected. At high latitude sites such as Spitsbergen (79°N) and Alert (82°N) (Rockmann et al., 2002) the amplitude of the OH seasonal cycle is greater than Indianapolis' (39°N) and will drive stronger variations in CO mole fraction, $\delta^{13}\text{C}$ (via OH sink fractionation and the seasonally-variable $\delta^{13}\text{C}$ -depleted CH_4 oxidation source) and $\delta^{18}\text{O}$ (mainly via OH sink fractionation). At Mount Sonnbllick (47°N), the OH seasonal variability is slightly larger than at Indianapolis, but the largest difference is a result of elevation. Mount Sonnbllick is well above the boundary layer at 3106 m above sea level (Gros et al., 2001), whereas Indianapolis is specifically sampled within the boundary layer. Therefore, in contrast to these other two studies (Gros et al., 2001; Rockmann et al., 2002), none of the tower sites in our study represent truly unpolluted locations. Anthropogenic signals at these sites (and especially at Towers 2 and 3) are an important component of the variability and may obscure the natural seasonal signals.

3.2 Winter 2013/2014 and winter 2014/2015 tower measurements

The tower data were analyzed over both winter periods using the regression approach described in Section 2.3 to determine the source CO isotopic signature and identify the dominant CO sources within the city (Figure 3). We note the average CO mole fraction urban enhancements are 27 nmol:μmol during the winter (Figure 2). Because these enhancements are relatively low compared to the background mole fractions, it is necessary to quantitatively remove the variable background in order to study the urban emission signals. The plots are strongly linear ($r^2 = 0.86 - 0.98$) indicating a consistent source isotopic signature for urban CO. The regressions provide $\delta^{13}\text{CO}$ values of $-27.7 \pm 0.45\text{‰}$ and $\delta\text{C}^{18}\text{O}$ values of $17.7 \pm 1.1\text{‰}$ for the urban CO source detected at both Tower 2 and Tower 3 (Figure 3). The two towers yield very similar source signatures, indicating that a common source type influences both towers, despite the different locations and footprints of the two tower locations. However, we investigate all

possible sources in the following sections to determine if multiple sources can explain the tower results.

3.3 Traffic study

The limited traffic study we performed produced too few measurements to be able to draw any strong conclusions. However, in this section, we examine the data and note several observations that may explain the results we have obtained. The linear regression analyses (same type of analyses as described in section 2.3) from the traffic study PFP's conducted in March 2015 are shown in **Figure 4**. One of the PFP samples captured a very high CO enhancement ($\sim 2800 \text{ nmol}\cdot\text{mol}^{-1}$) (**Figure 4**). The remaining traffic CO enhancements are generally between

200 and $500 \text{ nmol}\cdot\text{mol}^{-1}$ in the PFP's, and the isotopic values calculated using equation (6) are variable, ranging between -14.9‰ and -29.9‰ for $\delta^{13}\text{C}$ and 15.5‰ to 26.7‰ for $\delta\text{C}^{18}\text{O}$.

The linear regression analyses of the traffic study PFP sample source isotopic signatures were leveraged strongly by the sample with the highest CO enhancement (**Figure 4**). When all points were considered, the regressions produced a $\delta^{13}\text{C}$ value of $-28.7 \pm 0.1\text{‰}$ and a $\delta\text{C}^{18}\text{O}$ value of $15.7 \pm 0.3\text{‰}$. The same result was obtained (within 1σ) when any of the lower CO enhancement points was removed from the regression. When the highest CO enhancement sample was removed from the regression, the results were quite different: $-22.8 \pm 0.1\text{‰}$

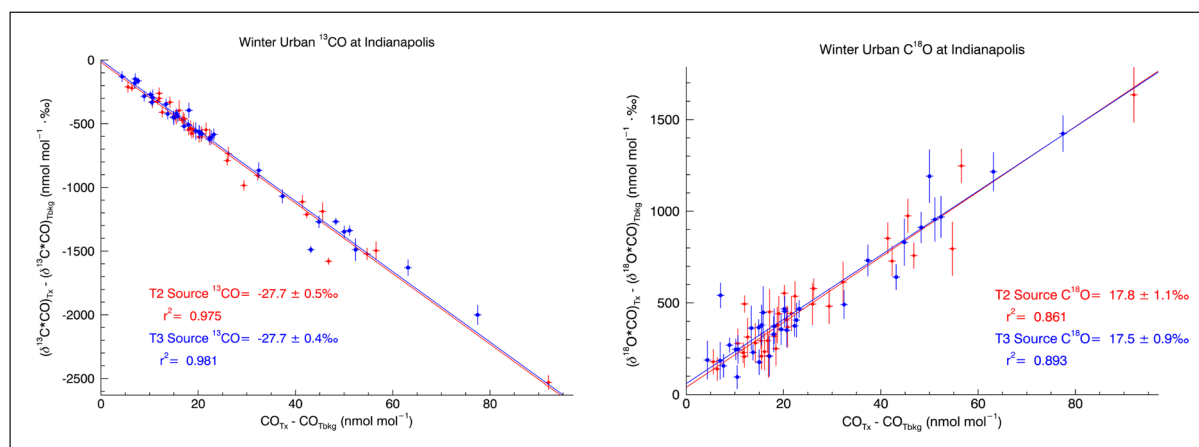


Figure 3: Ordinary Least Squares (OLS) regression analyses. CO isotopic data from November 2013/2014, December 2013/14, January 2014/2015 and February 2015. Tower 2 (T2) is in red, and Tower 3 (T3) is in blue. Analysis was done using a Monte Carlo Approach. The slope is the mean of 10,000 linear regressions run on the data using a normal probability distribution for each point based on the 1σ measurement error at that point. The uncertainty on the slope is 1 standard deviation calculated from the 10,000 slopes. For both towers and both isotopes, the linear model is an excellent fit ($r^2 \geq 0.86$). The error bars are the propagated measurement uncertainties for the given isotope and CO mole-fraction. The left panel shows the ^{13}C regression results, and the right panel shows the ^{18}O regression results. DOI: <https://doi.org/10.1525/elementa.136.f3>

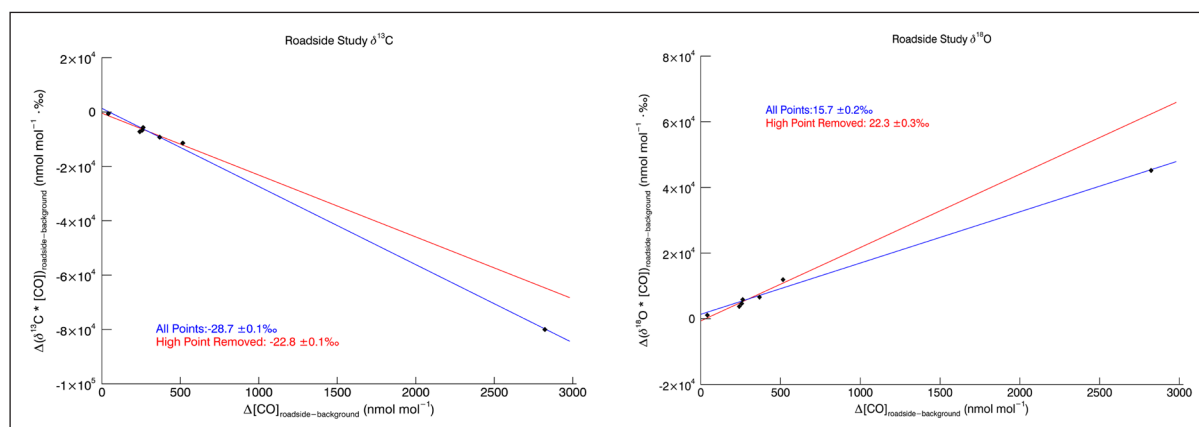


Figure 4: Traffic Study Isotopic Signatures. Regression analysis of the traffic study values. The red line shows the slope of the traffic values if the high mole fraction point is removed. The blue line shows the regression slope if the high value is included. The uncertainty for the blue line is the standard deviation of the slopes for 5 regression analyses, where one point is removed each time (except the high mole fraction point). The uncertainty for the red line is the standard deviation of 5 regression analyses, where the high mole fraction point is always removed. For four of the analyses, one of the lower mole fraction points was removed each time, and for the fifth, all of the lower mole fraction points were used. The left panel shows the ^{13}C regression results, and the right panel shows the ^{18}O regression results. DOI: <https://doi.org/10.1525/elementa.136.f4>

for $\delta^{13}\text{C}$ and $22.3 \pm 0.3\text{‰}$ for $\delta^{18}\text{O}$. The single, highly polluted point is dominating the overall isotopic signature of this regression, yet including it yields source isotopic signatures similar to our tower analysis. This is not conclusive, but is consistent with the hypothesis that a relatively small number of highly polluting vehicles could dominate the regression analysis in our tower data as well. The given uncertainties for the traffic data are 1σ , based on the 10,000 slopes run during the respective monte carlo simulation. This method likely underestimates the true uncertainty of these values because of the limited number of data points.

Applying Equation 6 for the high CO enhancement sample alone yields $-28.4 \pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $16.1 \pm 0.2\text{‰}$ for $\delta^{18}\text{O}$. We hypothesize that this high-CO sample may be the result of a vehicle or vehicles with inoperable catalytic systems, based on the isotopic values of uncatalyzed exhaust reported by other studies (Table 1). We stress that the estimated uncertainties on both the regression slope analyses and the single, high CO enhancement point are likely underrepresented because of the very small number of samples, and therefore this result should only be considered in the roughest possible sense.

The small size of the PFP traffic study data set precludes definitive conclusions about the associated CO isotopic signatures. However, some cursory observations are possible. First, the sample with the highest CO enhancement has a $\text{CO}_{\text{enh}}:\text{CO}_{2\text{enh}}$ ratio (R_{CO}) that is six times higher than that of the other traffic study samples ($47.1 \text{ nmol}:\mu\text{mol}$ and $7.5 \text{ nmol}:\mu\text{mol}$ respectively) (Table S4). Most of the carbon emitted from vehicles is

CO_2 , so R_{CO} provides a metric for catalytic system efficacy. Bishop and Stedman (2008, 2014) and Bishop et al. (2016) show that over time, vehicles emissions control systems degrade, and the vehicles progressively emit more CO. Therefore, older vehicles, particularly with higher mileage, can have a higher R_{CO} than newer vehicles (Bishop et al., 2016). In addition, Bishop et al. (2012) and Bishop and Stedman (2013) show that older vehicles or vehicles in disrepair account for less than 1% of the vehicle fleet yet produce up to a third of the CO emissions. Although results from a single sample cannot be considered conclusive, they are consistent with the hypothesis that the overall Indianapolis CO source signature may be dominated by a relatively small number of vehicles without properly functioning catalytic converters.

We further investigated the traffic R_{CO} by analyzing the continuous CRDS data from the traffic analysis. We observed a large amount of scatter in R_{CO} , which is expected because of contributions from vehicles with catalytic systems of a range of efficiencies. Despite the scatter, we can again make cursory observations about the R_{CO} produced by traffic, though we cannot make any definitive conclusions with these data. Turnbull et al. (2015) analyzed CRDS continuous data from the tower sites for Indianapolis, and estimated an approximate vehicle R_{CO} of $15 \text{ nmol}:\mu\text{mol}$. Turnbull et al. (2015) also show that linear regressions provide more realistic estimates than either the mean or median calculated using individual R_{CO} measurements. We estimated an overall traffic R_{CO} value of approximately $14 \text{ nmol}:\mu\text{mol}$ using a linear regression of the onroad and roadside observations (Figure 5). Because

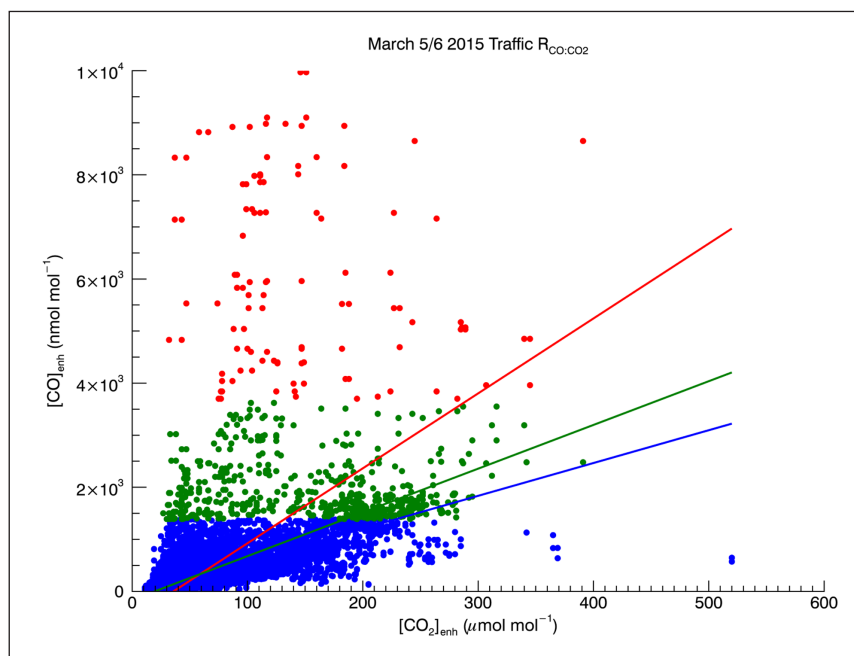


Figure 5: Traffic in situ CRDS CO:CO₂ Ratios. CO vs. CO₂ from the March 5 and 6, 2015 Traffic study. CO_{enh} and $\text{CO}_{2\text{enh}}$ indicate that background values have been subtracted from the traffic values. The red points represent the highest 1% of the CO measurements, the red and green points together represent the highest 5.5% of the CO measurements, and the blue points represent the lower 94.5% of the CO measurements. The lines are ordinary least squares bisector regressions. The red line represents the CO:CO₂ ratio for the entire data set ($\sim 14 \text{ nmol}:\mu\text{mol}$, $r^2 = 0.03$), the green line represents the CO:CO₂ ratio for 99% of the data ($\sim 8 \text{ nmol}:\mu\text{mol}$, $r^2 = 0.35$) and the blue line represents the CO:CO₂ ratio for 94.5% of the data ($\sim 6 \text{ nmol}:\mu\text{mol}$, $r^2 = 0.40$). DOI: <https://doi.org/10.1525/elementa.136.f5>

of the large scatter in R_{CO} , the regression fit from our traffic study used to determine R_{CO} was quite poor (r^2 of 0.03) (**Figure 5**). Two recent studies of vehicle emissions determined R_{CO} values of 5.68 ± 2.43 to 8.44 ± 0.45 nmol: μ mol in France (Ammoura et al., 2014) and 4.15 ± 0.3 nmol: μ mol in Switzerland (Popa et al., 2014). Bishop and Stedmann (2008, 2013) and Bishop et al., (2012) show that as catalytic technologies improve on vehicles through time, the R_{CO} of fleets in Los Angeles, CA, Denver, CO and Tulsa, OK have decreased from well over 15 nmol: μ mol to between 6 and 11 nmol: μ mol. In Baltimore, Maryland, roadside studies have found R_{CO} values of around 6 nmol: μ mol (Russell Dickerson, email/phone conversation, 2017). Because Bishop et al. (2012) and Bishop and Stedmann (2013) have found that 1% of the vehicle fleet can account for 30% of the CO emissions, we removed the highest 1% of the CO CRDS points and performed a regression on the remaining 99% (**Figure 5**). We obtained an R_{CO} of 8.4 ± 0.1 nmol: μ mol and a better fit for the regression (r^2 of 0.35). In order to achieve a value similar to Baltimore, MD of 6 nmol: μ mol (r^2 of 0.40) we needed to remove the highest 5.5% of the CO data (**Figure 5**). In all of these cases, the r^2 values are so low that these observations are cursory at best. However, if this result should hold true in a more in-depth traffic study, it suggests that the Indianapolis fleet may contain 4 to 5% more vehicles with large CO emissions relative to Baltimore. We again stress that this is a cursory observation, which provides one possible explanation for the traffic study data, and should not be considered a definitive result.

Further, our results are not directly comparable to the previous studies in France or Switzerland because the two European studies were conducted inside tunnels. It is well established (e.g. De Fré et al., 1994; Ropkins et al., 2009; Smit et al., 2017) that tunnel studies are superior to roadside or freeway measurements in capturing solely vehicle fleet emissions in a controlled environment, but may underestimate emissions due to the difference of driver behavior in tunnels vs. open roadways. It is difficult to know the extent, if any, the tunnel studies in France and Switzerland would differ from the open roadway (Ropkins et al., 2009). However, Smit et al. (2017) suggest that emissions of CO and other pollutants may be decreased in tunnels due to typical tunnel driving behavior being uncongested, smooth, high speed driving. Therefore, we speculate that the congested value of R_{CO} (8.44 ± 0.45 nmol: μ mol) from Ammoura et al. (2014) could be more representative of urban, open roadway traffic. This estimate is still significantly below both our traffic R_{CO} (~ 14 nmol: μ mol) and the traffic R_{CO} estimated from tower observations (15 nmol: μ mol) (Turnbull et al., 2015).

While the large uncertainties in these analyses do not allow definitive conclusions, our results are nevertheless consistent with the hypothesis that the vehicle fleet in Indianapolis is producing significantly more CO than contemporary fleets in Europe or in US cities with vehicle emission requirements (Indianapolis does not regulate vehicle CO emissions). The overall traffic R_{CO} is consistent with previous studies in which highly polluting vehicles

comprise a greater percentage of the overall fleet. Further, the traffic study source isotopic values agree with both our tower results and the values of uncatalyzed exhaust reported by Tsunogai et al. (2003) within uncertainty. These analyses support, but do not confirm, the hypothesis that vehicles with non-functioning or poorly functioning catalytic systems may be dominating the wintertime CO budget in Indianapolis.

3.4 Overview of likely wintertime sources of CO in Indianapolis

We hypothesize that mobile emissions from fossil fuel combustion are likely the main source of CO at Indianapolis during the winter, based on the results of Turnbull et al. (2015) as well as on our isotopic results from tower and traffic study samples. Unlike combustion of fuels for heating, we assume this source is consistent throughout the year, though it is expected to vary diurnally and throughout the week: higher CO emissions on weekdays (Monday–Friday) and lower emissions on weekends (Saturday and Sunday) (Turnbull et al., 2015). However, while the CO and CO₂ mole fractions measured at the tower sites will be lower on weekends as compared to weekdays, if other sources of CO are small, the CO:CO₂ ratio of the urban source should remain constant. Turnbull et al. (2015) calculated the CO, CO₂ and CO:CO₂ ratio enhancements using in situ CRDS measurements for each hour during weekdays and weekends from November–April at Indianapolis between 2011 and 2014. They found that the CO:CO₂ ratio didn't vary significantly between the weekdays and weekends ($\sim 7 \pm 1$ nmol: μ mol for the weekday/weekend analyses). Unfortunately, our isotopic data contains relatively few weekend results compared to weekday results. This precludes a robust analysis of the weekday/weekend isotopic effects. Therefore, we cannot say conclusively if any weekday/weekend effect is present in the isotopic data and must rely on the CO:CO₂ ratio results from Turnbull et al. (2015) discussed above.

Another likely source of CO during the winter months is combustion as a heat source. Taken together, combustion of fossil fuels and biomass for heating purposes are estimated to contribute $\sim 3\%$ of the annual Indianapolis CO emissions (EPA NEI 2011; Turnbull et al., 2015). However, since burning of fuels for heat is realistically only done during the colder months, this could account for $\sim 6\%$ or more of winter CO emissions at Indianapolis. Approximately two-thirds of residential and commercial heating at Indianapolis is by natural gas combustion and the remaining third is assumed to be electrical (Gurney et al., 2012). Even though biomass burning is not considered to be a significant source of CO₂ in Indianapolis (Gurney et al., 2012), the CO:CO₂ ratio (R_{CO}) in biomass burning is much greater than it is for other forms of combustion ($R_{CO} > 64$ nmol: μ mol for biomass burning vs ~ 8 nmol: μ mol for fossil fuel combustion) (Andreae and Merlet, 2001; Turnbull et al., 2015; Yates et al., 2016). Therefore, biomass burning for heat could still be a significant source of CO during the winter.

Another possible source of CO is electrical power generation via fossil fuel combustion. However, strong

pollution controls mean that the Harding Street Power Plant (the main power generation plant in Indianapolis) is estimated to produce only $\approx 0.5\%$ of the city's annual CO emissions (Turnbull et al., 2015). Because this source accounts for such a small fraction of the total emissions, we are not able to resolve changes in emissions from this plant within the uncertainty of our measurements.

3.5 Assessment of CO emissions from natural gas combustion for heating purposes

To explore the hypothesis that heating-related CO emissions could be a significant wintertime source, we analyzed the tower $\delta^{13}\text{C}$ CO data with respect to temperature. As mentioned earlier, natural gas is used for two thirds of residential and commercial heating (Gurney et al., 2012). Detailed gas usage statistics for Indianapolis are not available, and due to the sampling frequency of our isotopic data, monthly averaged gas usage data are not sufficient to correlate with our isotopic results. However, monthly gas usage data for the state of Indiana clearly show that natural gas consumption increases dramatically at colder temperatures, with nearly 10x higher use during the winter as compared to the summer (http://www.eia.gov/dnav/ng/ng_sum_lsum_dcu_sin_m.htm; supplemental material, Figure S3). Lamb et al. (2016) found that natural gas used in Indianapolis is about 95% methane, and thus methane will be the dominant precursor for CO during natural gas combustion. Methane in natural gas has an average carbon isotopic signature of -44‰ (Whiticar, 1990; Kato et al., 1999). While the $\delta^{13}\text{C}$ CO from methane combusted for heating purposes has not been previously measured, Kato et al. (1999) measured $\delta^{13}\text{C}$ CO produced

from methane combusted by natural gas busses and found a value of $-51.3 \pm 1.5\text{‰}$. Both this value and the $\delta^{13}\text{C}$ of the source methane (-44‰) are strongly depleted in ^{13}C relative to the $\delta^{13}\text{C}$ CO previously measured in traffic emissions (-24‰ to -29‰ ; **Table 1**). Therefore, if heating-related CO emissions are an important component of the urban CO source, we would expect a decrease in $\delta^{13}\text{C}$ CO_s as heating demand goes up on colder days. We note that while CO_{enh} at the towers would be affected by wind speed and direction as well as boundary layer height, calculated $\delta^{13}\text{C}$ CO_s should not be affected by these parameters as long as the sources are widely distributed throughout the city (as is the case for residential/commercial heating and traffic).

Our urban $\delta^{13}\text{C}$ CO_s results show no correlation with temperature (**Figure 6**). Thus, while combustion of natural gas for heat may produce some CO, its effect appears to be insignificant. Further, if natural gas combustion were a large source of CO, the time series for $\delta^{13}\text{C}$ CO at the polluted towers (**Figure 2**) would be shifted toward more negative values relative to the background tower (Tower 1) during the winter months. This is not evident from the time series, consistent with the conclusion that large increases in natural gas usage in the winter do not significantly impact the Indianapolis CO budget. Further, because natural gas emissions would vary differently than other sources, we would expect to see much greater scatter in our tower data (**Figure 3**) if natural gas produced CO was significant.

We can estimate an upper bound on natural gas heating CO emissions based on our $\delta^{13}\text{C}$ CO results. For this estimate, we assume that 1) mobile emissions are the dominant source, 2) $\delta^{13}\text{C}$ CO_{mobile} is equal to $\delta^{13}\text{C}$ CO_s (the

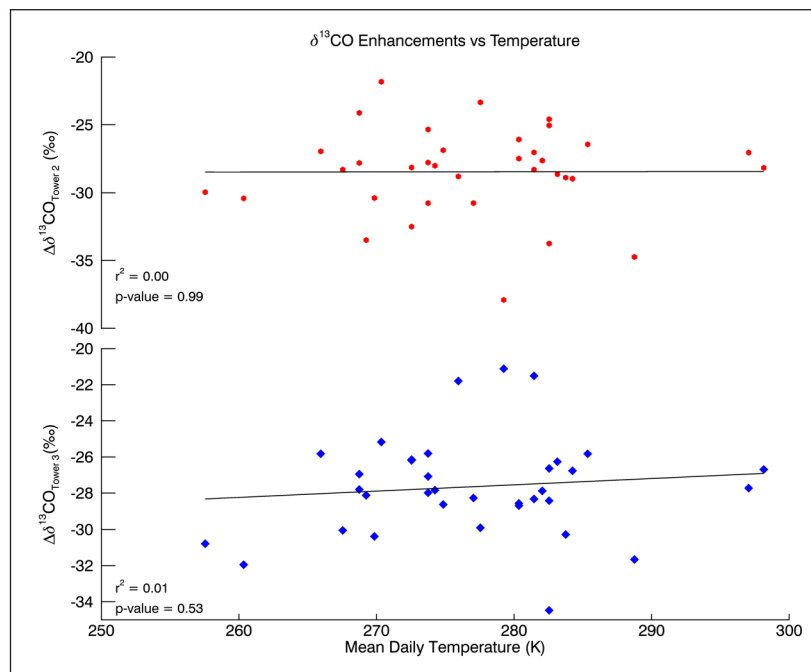


Figure 6: $\delta^{13}\text{C}$ CO vs Temperature. $\Delta\delta^{13}\text{C}$ plotted against ambient temperature at the time of measurement. $\Delta\delta^{13}\text{C}$ indicates that the d value has been calculated according to equation (6) such that the background has been removed. No correlation between temperature and $\delta^{13}\text{C}$ indicates that the source sectors do not change significantly with temperature, suggesting heating does not contribute significantly to the CO budget. The top panel shows tower 2 ^{13}C vs temperature, and the bottom panel shows tower 3 ^{13}C vs temperature. DOI: <https://doi.org/10.1525/elementa.136.f6>

overall $\delta^{13}\text{CO}$ of the urban source), and 3) CO emissions from CH_4 combustion do not affect $\delta^{13}\text{CO}$ beyond the uncertainty bounds. We use a simple mass balance approach:

$$\delta^{13}\text{CO}_{s,\text{min}} = (f_{\text{mobile}})\delta^{13}\text{CO}_{\text{mobile}} + (f_{\text{CH}_4\text{combustion}})\delta^{13}\text{CO}_{\text{CH}_4\text{combustion}} \quad (7)$$

$$f_{\text{CH}_4\text{combustion}} + f_{\text{mobile}} = 1 \quad (8)$$

where $\delta^{13}\text{CO}_{s,\text{min}}$ is -28.7‰ , our overall source minimum $\delta^{13}\text{CO}$ at the 2σ bound of its uncertainty, and f denotes the fractional contribution from each source, $\delta^{13}\text{CO}_{\text{mobile}}$ is $-27.7 \pm 0.5\text{‰}$ and $\delta^{13}\text{CO}_{\text{CH}_4\text{combustion}}$ is varied between $-44\text{‰} \pm 1.5\text{‰}$ and $-51.3 \pm 1.5\text{‰}$ as discussed above (Kato et al., 1999).

We solve these equations for $f_{\text{CH}_4\text{combustion}}$:

$$f_{\text{CH}_4\text{combustion}} = \frac{(\delta^{13}\text{CO}_{s,\text{min}} - \delta^{13}\text{CO}_{\text{mobile}})}{(\delta^{13}\text{CO}_{\text{CH}_4\text{combustion}} - \delta^{13}\text{CO}_{\text{mobile}})} \quad (9)$$

Using these values, we obtain a range for $f_{\text{CH}_4\text{combustion}}$ between 0.04 and 0.06 for the 2σ upper bound of the contribution of wintertime CH_4 combustion for heat to the overall CO source. Because these calculations only consider the winter data, the 4–6% range is, at most, valid for the colder 6 months of the year, which translates to a yearly upper limit of $\sim 2\text{--}3\%$. This is in agreement within uncertainties with the EPA NEI 2011 estimation of 2–3% for annually averaged CO contributions from natural gas heating. However, due to the above-mentioned assumptions about the $\delta^{13}\text{CO}$ of the CO produced by combustion in heating furnaces, this result should be considered a rough estimate, and not as a definitive assessment of natural gas produced CO.

3.6 Assessment of CO emissions from biomass combustion for heating purposes

The isotopic signatures of CO from biomass burning for heat are similar to that of our tower measurements (Table 1, Figure 3). Biomass burning thus cannot be easily distinguished from other sources using CO isotopes. However, biomass burning has a large R_{CO} (>60 nmol/mmol) relative to fossil fuel combustion (~ 7 nmol/mmol) (Andreae and Merlet, 2001; Turnbull et al., 2015; Yates et al., 2016). Because of this large difference between the fossil fuel and biomass combustion $\text{CO}:\text{CO}_2$ ratios, we attempted to determine the $\text{CO}:\text{CO}_2$ ratio for the CO and CO_2 enhancements during the winter months and compare this to other studies in which $\text{CO}:\text{CO}_2$ ratios were measured for biomass burning and fossil fuels (Turnbull et al., 2015; Yates et al., 2016) (supplemental material, section 6). However, this analysis did not produce useful results. The analysis is highly sensitive to the $\text{CO}:\text{CO}_2$ ratios used for different combustion sources, which are not known precisely enough for this study (supplemental material, section 6). Further, the scatter in our data leads to large uncertainties in the calculated regression slopes.

Instead, we must rely on other studies to assess the amount of CO that is likely produced in Indianapolis

during the winter. The EPA NEI 2011 reports biomass burning emissions to be almost entirely from residential heating, and estimates the total impact of all biomass and natural gas heating to be 3% of the yearly CO budget. Above, we calculated natural gas heating emissions to be 2–3% of the yearly budget, suggesting that biomass burning emissions account for 0–1% annually. In addition, Gurney et al. (2012) estimated residential and commercial heating to be two thirds natural gas and one third electrical, and does not attribute any heating to biomass burning. Based on these studies and our calculations, we assume biomass burning in Indianapolis is unlikely to be a significant source of CO.

3.7 Mobile emissions as the dominant source of urban CO

Our analyses above rule out atmospheric reactions as a significant wintertime CO source in Indianapolis and suggest heating-related combustion contributes at most 4–6% to the CO budget during winter. This leaves mobile emissions of CO as the only major source. However, the δ_s values for ^{13}CO ($-27.7 \pm 0.5\text{‰}$) and C^{18}O ($17.7 \pm 1.1\text{‰}$) determined from tower measurements at Indianapolis are not entirely consistent with other recent estimates of fleet-wide traffic emissions (Table 1).

Fleet-wide measurements in past studies have given a range of values for $\delta^{13}\text{CO}$ of -28.8‰ to -23.8‰ and $\delta\text{C}^{18}\text{O}$ of 20.7‰ to 24.6‰ (Stevens et al., 1972; Kato et al., 1999; Tsunogai et al., 2003; Popa et al., 2014). Our δ_s values for Indianapolis are on the low end of the reported range for $\delta^{13}\text{CO}$ and below the reported range for $\delta\text{C}^{18}\text{O}$. However, studies that directly sampled tail pipe CO emissions (Tsunogai et al., 2003; Kato et al., 1999) show that individual vehicles' isotopic signatures can significantly differ from the fleet aggregate isotopic signatures. Popa et al. (2014) summarize the variability in isotopic signatures for different vehicles, noting that both the carbon and oxygen ratios tend to be depleted in ^{13}CO and C^{18}O for vehicles with inoperable catalytic systems, relative to vehicles with operational units.

Indianapolis (and most of Indiana) does not require that vehicles operated within its borders use any form of emission control system, including catalytic converters (<http://www.in.gov/bmv/2655.htm>). While new vehicles sold and operated in Indianapolis will initially have functional catalytic systems, this lack of emission regulation suggests that more vehicles operated within Indianapolis could have poorly functioning or non-functioning catalytic systems than in previously studied urban regions with more emission regulation (e.g. Popa et al., 2014). Unfortunately, because there are no emissions regulations in Indianapolis, there are also no records of tailpipe emissions for individual vehicles.

However, using the National Household Travel Survey 2009 (NHTS 2009), generated by the US Department of Transportation's Federal Highway Administration (<http://nhts.ornl.gov>), prior results published by Bishop and Stedman (2014), and studies by IHS Automotive (<http://news.ihsmarket.com/press-release/automotive/average-age-light-vehicles-us-rises-slightly-2015-115-years-ihs>

reports), we are able to make some inferences about the fleet age in Indianapolis. Bishop and Stedman (2016) show that as a car's mileage increases, its catalytic efficiency declines. Using the NHTS 2009 study, we found a mean vehicle age of nine years for Indianapolis in 2008 (<http://nhts.ornl.gov>). Bishop and Stedman (2014) show that the economic recession of 2008 caused the vehicle fleet age to begin to rise relative to pre-2008 mean fleet age. IHS Automotive research shows that in 2015, the US mean fleet age reached 11.5 years (<http://news.ihsmarket.com/press-release/automotive/average-age-light-vehicles-us-rises-slightly-2015-115-years-ihs-reports>).

Further, in cities such as Tulsa, OK and Van Nuys, CA, just 1% of the vehicle fleet accounts for as much as a third of the total CO emissions, and these “high emitters” are generally older model year vehicles (Bishop et al., 2012; Bishop and Stedman, 2013). These high emitters are shown to strongly influence CO emissions in Van Nuys (A suburb of Los Angeles, CA), where vehicles must meet California's strict emission standards every two years in order to be registered (<http://www.dmv.org/ca-california/smog-check.php>). In contrast, the lack of emission regulation in Indianapolis means that high emitters are free to operate indefinitely within the city limits without repair. We found higher CO:CO₂ ratios in our traffic study (14.4 ± 0.5 nmol:μmol) relative to recent studies in other cities (section 3.3), which is expected if high emitting vehicles comprise a larger percentage of Indianapolis traffic. This result agrees with estimates from the Indianapolis tower measurements by Turnbull et al. (2015) (15 nmol:μmol). The increase in fleet age in the US, the lack of emission regulation in Indianapolis, and the high CO:CO₂ ratios from traffic make it plausible that “high emitters” represent a larger portion of the Indianapolis fleet than in more emission-regulated cities.

Kato et al. (1999) and Tsunogai et al. (2003) showed that vehicles without catalytic converters emit more CO and that this CO has significantly different isotopic signatures (**Table 1**) than vehicles with functional catalytic systems (Bishop and Stedman, 2008). By producing more CO per kg fuel used (Bishop and Stedman, 2008; Bishop et al., 2016), the uncatalyzed vehicles can strongly influence the fleet-wide CO isotopic signature. Our fleet-wide estimates of δ_s from the tower measurements (**Figure 3**) most closely resemble the uncatalyzed gasoline engine results from the tail pipe study by Tsunogai et al. (2003). We note that our isotopic analysis system has not been inter-calibrated with the laboratories cited in **Table 1**. However, measurements of different emitters from within a single lab will not suffer from any calibration offsets. For a given study of traffic emissions (Tsunogai et al., 2003; Kato et al., 1999), uncatalyzed exhaust is always lighter in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ than catalyzed exhaust. In our study, the δ_s estimates from tower measurements ($\delta^{13}\text{C} = -27.7 \pm 0.5\text{‰}$ and $\delta^{18}\text{O} = 17.7 \pm 1.1\text{‰}$) are also similar to the highly polluted sample in our traffic study ($\delta^{13}\text{C} = -28.4 \pm 0.1\text{‰}$ and $\delta^{18}\text{O} = 16.1 \pm 0.2\text{‰}$), but differ from the “typical” traffic values when the highly polluted sample is removed ($\delta^{13}\text{C} = -22.8 \pm 0.1\text{‰}$ and $\delta^{18}\text{O} = 22.3 \pm 0.2\text{‰}$). We therefore hypothesize that emissions from a relatively

small fraction of vehicles without functional emission controls may dominate the Indianapolis wintertime CO budget. We note that other engine malfunctions could theoretically cause vehicles to produce more CO as well; however, we do not have literature values for isotopic signatures of CO from vehicle exhaust for vehicles with engine malfunctions.

4. Conclusions

We performed stable isotopic analysis of CO on samples taken from three tall towers at Indianapolis, Indiana over two winters and constrained the wintertime urban isotopic signatures: $-27.7 \pm 0.5\text{‰}$ (VPDB) for $\delta^{13}\text{C}$ and $17.7 \pm 1.1\text{‰}$ (VSMOW) for $\delta^{18}\text{O}$. One of the towers was used as a background site, allowing for the first time unambiguous separation of urban emission CO, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ signals from background air. Due to the small distances between towers, we were able to discount CO sources and sinks from atmospheric oxidative chemistry. Our regression analyses of the CO source isotopic signature provided strong linear fits to the isotopic data ($r^2 \geq 0.86$ in all cases). This is only possible if there is a single source, or multiple sources with a single isotopic signature. While our secondary analyses cannot fully rule out significant contributions from other anthropogenic sources, they nonetheless suggest that CO emissions from natural gas and biomass combustion are small, leaving vehicular emissions as the primary wintertime CO source in Indianapolis.

Our Indianapolis source isotopic signature results ($-27.7 \pm 0.5\text{‰}$ (VPDB) for $\delta^{13}\text{C}$ and $17.7 \pm 1.1\text{‰}$ (VSMOW) for $\delta^{18}\text{O}$) are in good agreement with estimates of uncatalyzed gasoline exhaust measured by Tsunogai et al. (2003), but differ from most other estimates of fleet-wide traffic CO isotopic signatures (Stevens et al., 1972; Kato et al., 1999; Popa et al., 2014) (**Table 1**). Further, the vehicle R_{CO} calculated at Indianapolis in our traffic study, as well as by Turnbull et al. (2015) suggests that traffic in Indianapolis, which lacks emission regulations, is producing significantly more CO than traffic in emission-regulated cities of Baltimore (US), Paris (France), or Zurich (Switzerland). The results are thus consistent with the hypothesis that vehicles without functional catalytic systems dominate the Indianapolis urban CO budget.

Turnbull et al. (2015) estimated mobile emissions to be 87% of the total CO budget at Indianapolis. While our study has large uncertainty in the source attribution from our secondary analyses, it is possible that this estimate is too low for the winter months, and traffic may in fact account for as much as 96% which is in close agreement with the EPA NEI (2011). However, further work is needed to confirm this assessment.

The difference between our isotopic results and those from prior studies highlights the need for continued CO isotopic monitoring. Changing traffic fleets are expected to continue to drive changes in both CO emission rates and their isotopic signature. Regional differences in regulation and fuel type will influence the isotopic signatures of fossil fuel combustion, as this study has suggested for Indianapolis.

Data Accessibility Statement

Data for this paper is contained in the supplemental material in Table S5.

Supplemental File

The supplemental file for this article can be found as follows:

- **Text S1.** Carbon monoxide isotopic measurements in a US urban center constrain Indianapolis isotopic signatures and suggest mobile fossil fuel emissions as the dominant wintertime source. DOI: <https://doi.org/10.1525/elementa.136.s1>

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Competing interests

The authors have no competing interests to declare.

Author contributions

- Contributed to conception and design: IJV, VVP, JCT, PFP, JWCW, BHV, KG, RP, CS
- Contributed to acquisition of data: IJV, VVP, JCT, PFP, AK, NLM, SJR
- Contributed to analysis and interpretation of data: IJV, VVP, JCT, KG
- Drafted and/or revised the article: IJV, VVP, JCT, NLM, CS
- Approved the submitted version for publication: All

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