



# Large and seasonally varying biospheric CO<sub>2</sub> fluxes in the Los Angeles megacity revealed by atmospheric radiocarbon

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Measurements of  $\Delta^{14}\text{C}$  and CO<sub>2</sub> can cleanly separate biogenic and fossil contributions to CO<sub>2</sub> enhancements above background. Our measurements of these tracers in air around Los Angeles in 2015 reveal high values of fossil CO<sub>2</sub> and a significant and seasonally varying contribution of CO<sub>2</sub> from the urban biosphere. The biogenic CO<sub>2</sub> is composed of sources such as biofuel combustion and human metabolism and an urban biospheric component likely originating from urban vegetation, including turf and trees. The urban biospheric component is a source in winter and a sink in summer, with an estimated amplitude of 4.3 parts per million (ppm), equivalent to 33% of the observed annual mean fossil fuel contribution of 13 ppm. While the timing of the net carbon sink is out of phase with wintertime rainfall and the sink seasonality of Southern California Mediterranean ecosystems (which show maximum uptake in spring), it is in phase with the seasonal cycle of urban water usage, suggesting that irrigated urban vegetation drives the biospheric signal we observe. Although 2015 was very dry, the biospheric seasonality we observe is similar to the 2006–2015 mean derived from an independent  $\Delta^{14}\text{C}$  record in the Los Angeles area, indicating that 2015 biospheric exchange was not highly anomalous. The presence of a large and seasonally varying biospheric signal even in the relatively dry climate of Los Angeles implies that atmospheric estimates of fossil fuel–CO<sub>2</sub> emissions in other, potentially wetter, urban areas will be biased in the absence of reliable methods to separate fossil and biogenic CO<sub>2</sub>.

radiocarbon | urban | carbon dioxide

Megacities, urban regions with populations >10 million, are global foci of both population and CO<sub>2</sub> emissions from combustion of fossil fuels. As of 2005, it is estimated that global CO<sub>2</sub> emissions from these cities were 1.1 Pg C y<sup>-1</sup>, representing 12% of the global total (1). While just ~6% of the global population now resides in ~45 megacities, this population fraction is expected to increase throughout this century (2). As a result, global megacity emissions are forecast to reach 2.2 Pg C y<sup>-1</sup> by 2050 (1), a total larger than current emissions for any single country except China. Thus, determining megacity emissions and their trends will be an important element of any effort to assess the efficacy of emission mitigation strategies (3), especially because subnational political entities such as cities and states or provinces are emerging as key players in anthropogenic emissions mitigation efforts (e.g., C40 Cities).

Fossil fuel–CO<sub>2</sub> emissions are typically determined using economic statistics describing fossil fuel use and associated emissions factors and can be estimated at a variety of scales ranging from whole countries to individual buildings (4). These data can also yield detailed information on emissions from fossil fuel use in different sectors, such as on-road transportation, residential heating, and power generation. However, such “bottom-up” inventories often take time to compile and update

and frequently lack quantitative uncertainty estimates (e.g., ref. 5). In contrast, “top-down” approaches use distributed atmospheric measurements to estimate emissions. Although top-down studies tend to lack sectoral specificity, they implicitly include all possible sources within a geographic region. While top-down estimates may be subject to systematic errors in atmospheric transport (e.g., refs. 6, 7), interannual variability and trends of CO<sub>2</sub> fluxes are less likely to be impacted by systematic transport errors (8). Both bottom-up and top-down approaches have the potential to provide near real-time information to policy makers (9, 10) and, taken together, have the potential to provide complementary sectoral information and verifiable emissions totals.

A major challenge in top-down CO<sub>2</sub> emissions estimation is accurately partitioning fossil fuel and biospheric fluxes. Incorrect estimation of biospheric contributions can lead to equally

## Significance

Megacities contribute significantly to national and global CO<sub>2</sub> emissions and are an increasingly important element of emissions mitigation efforts. Atmospheric monitoring helps to characterize urban emissions, but CO<sub>2</sub> measurements alone cannot distinguish between biogenic and fossil fuel contributions to observed CO<sub>2</sub> enhancements. We use measurements of CO<sub>2</sub> and the fossil fuel tracer <sup>14</sup>CO<sub>2</sub> to demonstrate that even for highly urbanized and arid environments such as Los Angeles, the managed urban biosphere contributes significantly to the local carbon budget. These findings highlight the need to understand and quantify urban biospheric CO<sub>2</sub> in order to more accurately measure and track fossil fuel–CO<sub>2</sub> emissions and the impact of urban greening campaigns, as needed to evaluate and optimize emissions mitigation strategies.

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erroneous fossil fuel–CO<sub>2</sub> quantification (6), and vice versa. At continental to global scales, fossil fuel–CO<sub>2</sub> emissions are typically assumed to be perfectly known from inventories with any residual CO<sub>2</sub> signal assigned to the biosphere, although some studies have relaxed this assumption (6, 11–13). On the other hand, at the urban scale, many top-down CO<sub>2</sub> studies have assumed zero biospheric influence (14–19) or adopted model-based estimates of biospheric fluxes and then used atmospheric CO<sub>2</sub> measurements to determine the balance attributable to emissions from fossil fuel combustion (20–22). Despite recent advances in modeling urban biospheric CO<sub>2</sub> fluxes (23), their magnitude and variability remain poorly known. Accurately quantifying urban biospheric fluxes and their seasonal variation is essential because any deviation of true and modeled (or assumed) biospheric fluxes would be translated into an observational bias in the magnitude and, possibly, the year-to-year trends of derived fossil fuel–CO<sub>2</sub> emissions.

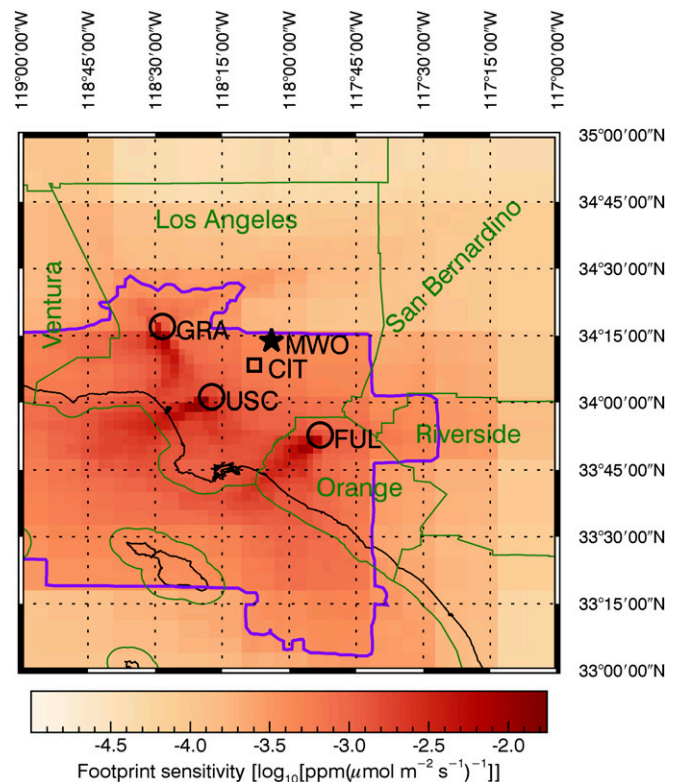
For Los Angeles (L.A.), a megacity spread over more than 15,000 km<sup>2</sup> with a population of ~18 million (*SI Appendix, Table S3*), both bottom-up and top-down studies are adding to our understanding of its substantial urban CO<sub>2</sub> fluxes. The Hestia–L.A. data product (4) quantifies fossil fuel–CO<sub>2</sub> emissions for five counties in the L.A. region down to the level of roads and individual buildings. Total emissions are estimated to be ~45 Tg C y<sup>-1</sup>, with the on-road (43%) and industrial (25%) sectors being the largest contributors. Atmospheric CO<sub>2</sub> monitoring as part of the Los Angeles Megacity Carbon Project (24) began in 2013 with the aim of estimating CO<sub>2</sub> emissions using a network of observation sites within and surrounding the megacity. However, Hestia–L.A. focuses exclusively on fossil fuel–CO<sub>2</sub> emissions, while L.A. megacity CO<sub>2</sub> measurements detect the total CO<sub>2</sub> flux (fossil plus biogenic). To date, there are also no available bottom-up models of urban biospheric CO<sub>2</sub> for the L.A. region. One previous study (25) simulated net biospheric CO<sub>2</sub> flux for the region, but assumed zero flux for the urban area. In general, simulating urban biospheric fluxes for L.A. is difficult, given the high spatial heterogeneity of the landscape combined with the paucity of urban flux measurements (e.g., chambers or eddy-flux towers) that would constrain model parameters relating to photosynthesis and respiration. Some previous studies focusing on fossil fuel–CO<sub>2</sub> in the L.A. area estimated biogenic CO<sub>2</sub> contributions, but they were either conducted over short periods (26) or used a single site of potentially limited representativity (27). CO<sub>2</sub> fluxes have also been calculated for L.A. using data from aircraft measurement campaigns (28) and remote sensing (18), but these studies made no attempt to account for biogenic contributions. Despite these studies, little is currently known about CO<sub>2</sub> fluxes from the urban biosphere in the L.A. megacity.

In this study, we interpret measurements of CO<sub>2</sub> mole fraction and their <sup>14</sup>C:C ratios (expressed as Δ<sup>14</sup>C) obtained from air samples collected two to three times per week over more than a year at three sites within the Los Angeles Megacity Carbon Project greenhouse gas network (24) (Fig. 1). Δ<sup>14</sup>C is a nearly unambiguous tracer for fossil fuel–CO<sub>2</sub> because, unlike all other CO<sub>2</sub> sources to the atmosphere, fossil fuel-derived CO<sub>2</sub> contains no <sup>14</sup>C (e.g., refs. 29, 30). Past urban studies have used measurements of CO<sub>2</sub> and Δ<sup>14</sup>C to estimate the contribution of fossil fuel combustion to observed CO<sub>2</sub> variation (e.g., refs. 27, 31–35), but here we focus on using atmospheric measurements to better understand the timing and origin of urban biospheric fluxes in the L.A. megacity. In contrast to inventories, models, or remote sensing observations, our data offer relatively direct measures of urban biospheric and fossil CO<sub>2</sub> fluxes. Our results show an unequivocal CO<sub>2</sub> signal originating from the urban biosphere, despite the density of the urban development and the naturally dry Mediterranean environment. Additionally, our Δ<sup>14</sup>C measurements show that CO<sub>2</sub> fluxes from the L.A. urban biosphere vary seasonally, with a timing best explained by managed urban

water use rather than precipitation. While our observations took place in a year of extreme drought, we suggest that the influence of managed water use on the urban biosphere may be a persistent feature of the associated CO<sub>2</sub> uptake response, occurring even in years when drought was less severe or absent.

## Methods

From November 2014 to March 2016, we used National Oceanic and Atmospheric Administration (NOAA) programmable flask packages (PFPs) and programmable compressor packages (36) to collect paired air samples at 2 PM local standard time at three existing Los Angeles Megacity Carbon Project sites: the corners of building rooftops at the University of Southern California (USC) and California State University, Fullerton (FUL) at 50 m above ground level, and from a 51-m tower in Granada Hills (GRA) (Verhulst, 2017 (24), *SI Appendix*). These sites were chosen to represent a broad swath of the most densely populated part of the L.A. Basin. We measured the CO<sub>2</sub> mole fraction on one member of PFP sample pairs returned to the NOAA Global Monitoring Laboratory. After measurement of other greenhouse gases on NOAA's high-precision/high-accuracy greenhouse gas measurement system (36), we extracted residual air from PFP flask pairs and isolated CO<sub>2</sub> for later <sup>14</sup>C measurement using established cryogenic techniques (37). We then graphitized pure CO<sub>2</sub> samples and sent them to the University of California, Irvine, Keck Accelerator Mass Spectrometry Facility for high-precision Δ<sup>14</sup>C measurement. We specify a one-sigma measurement uncertainty of ~1.8‰ based on repeat measurement of control samples (38), equivalent to ~1.2 parts per million (ppm) of recently added fossil fuel–CO<sub>2</sub> (*SI Appendix*). All CO<sub>2</sub> and Δ<sup>14</sup>C data are provided in *Dataset S1*. We



**Fig. 1.** Annual average footprint (surface flux sensitivity) for the three Los Angeles Megacity Carbon Project sampling sites used in this study (open circles). Green lines represent county boundaries. The purple line represents the 50% influence contour (50% of the total footprint influence is inside the contour). The full domain of the footprints (which go back 60 h) is from 121°W–114°W and 31.4°N–36.8°N and includes substantial portions of desert and ocean. Also note that the WRF-STILT footprint model decreases its resolution away from the sampling sites, as can be seen in the block-like nature of the footprints and contours. The star represents the high-altitude background site (MWO), and the square shows the location of Newman et al. (2016) Pasadena (CIT) samples discussed in the text (27).

calculated average surface sensitivities for all samples during the study period using 1.33-km resolution Weather Research and Forecasting model (WRF) meteorology (version 3.6.1) in conjunction with the Stochastic Time-Inverted Lagrangian Transport (STILT) back-trajectory model to create individual sample "footprints" with  $0.03^\circ \times 0.03^\circ$  resolution (39). The average footprints show that our midafternoon samples are sensitive to fluxes from large portions of the L.A. Basin, especially L.A. County (Fig. 1).

To quantify  $\text{CO}_2$  enhancements for L.A., we define representative background  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  levels based on nighttime (2 AM local standard time) measurements made at Mount Wilson Observatory (MWO, 1,670 m above sea level (m.a.s.l.); Fig. 1), when polluted L.A. Basin boundary layer air has typically descended, and the site samples the relatively clean, well-mixed free troposphere. Data quality control additionally excluded a few obvious low  $\Delta^{14}\text{C}$  outliers, corresponding to air with high fossil fuel- $\text{CO}_2$ . A total of 367 paired  $\Delta^{14}\text{C}$  and  $\text{CO}_2$  measurements at GRA ( $n = 115$ ), USC ( $n = 125$ ), and FUL ( $n = 127$ ) were also filtered to maximize the representativeness of the data. First, all samples associated with windspeeds less than  $1.5 \text{ m s}^{-1}$  were excluded from further analysis to avoid stagnant conditions (SI Appendix); second, in the case of USC and FUL, samples with wind directions corresponding to the building roof were excluded to minimize the possibility of contamination from rooftop exhaust vents, leaving 271 paired measurements for use in the remainder of the analysis. Individual  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  background values were created by fitting curves to the screened MWO data to permit resampling at the times of observations at GRA, USC, and FUL (Fig. 2). Other L.A.-area locations, such as San Clemente Island, may provide better representation of background air at certain times of year (24), but MWO is the only local background site with a high density of  $\Delta^{14}\text{C}$  measurements. Moreover, carbon monoxide (CO) measurements of the same nighttime MWO air samples used to construct the  $\Delta^{14}\text{C}$  background are similar to the Pacific marine boundary layer CO reference (40) at  $33^\circ\text{N}$  (SI Appendix, Fig. S1). This suggests that nighttime MWO measurements should provide a reliable representation of relatively clean background air coming from either on or off shore into the L.A. Basin. A previous fossil fuel- $\text{CO}_2$  study using  $\Delta^{14}\text{C}$  data from Pasadena (CIT) in the eastern part of the L.A. Basin (27) used Utqiagvik, AK (BRW)  $\Delta^{14}\text{C}$  data as a background, because measurements from nearby sites were not available. MWO should provide for improved representation of the local  $\Delta^{14}\text{C}$  background, given its proximity to the L.A. greenhouse gas monitoring sites and the similarity to off-shore records of CO.

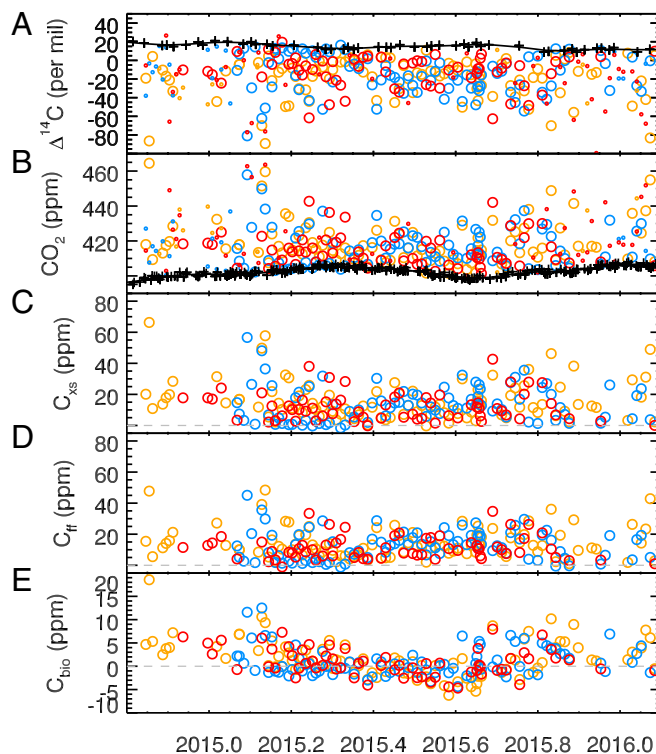
## Results and Discussion

Fig. 2 A and B show  $\Delta^{14}\text{C}$  and  $\text{CO}_2$  measurements for GRA, USC, and FUL in addition to background values and curve fits from MWO. Over the course of the study period,  $\text{CO}_2$  at the three sites was enhanced relative to background by  $14.6 \pm 11.8$  ppm (multisite mean and one-sigma SD). Mean  $\Delta^{14}\text{C}$  was depleted by  $-30.9 \pm 21.4\text{‰}$  relative to background, reflecting the substantial influence of  $^{14}\text{C}$ -free  $\text{CO}_2$  emissions from fossil fuel combustion. To better understand the relationship between  $\text{CO}_2$  enhancements and  $\Delta^{14}\text{C}$  depletions, we first performed an isotopic mixing analysis (41) using data from all three sites (Fig. 3). We start from mass balance equations for  $\text{CO}_2$  and its isotopic composition (Eqs. 1 and 2) (30), where  $\text{CO}_2$  mole fractions and  $\Delta^{14}\text{C}$  values are abbreviated as C and  $\Delta$ ; "obs" are GRA, USC, and FUL observations of either C or  $\Delta$ ; "bg" is the interpolated MWO background; "ff," "r," and "p" represent the fossil fuel, respiratory, and photosynthetic mole fraction contributions modifying the background; and "xs" represents the sum of all such contributions above or below background.

$$C_{\text{obs}} = C_{\text{bg}} + C_{\text{ff}} + C_r + C_p = C_{\text{bg}} + C_{\text{xs}} \quad [1]$$

$$\Delta_{\text{obs}} C_{\text{obs}} = \Delta_{\text{bg}} C_{\text{bg}} + \Delta_{\text{ff}} C_{\text{ff}} + \Delta_r C_r + \Delta_p C_p = \Delta_{\text{bg}} C_{\text{bg}} + (\Delta \times C)_{\text{xs}} \quad [2]$$

In order to provide a first-order estimate of the average biogenic and fossil  $\text{CO}_2$  contributions to  $C_{\text{xs}}$ , we regress  $C_{\text{xs}}$  vs.  $(\Delta \times C)_{\text{xs}}$ , where the slope,  $\Delta_{\text{source}}$ , is the flux-weighted average isotopic signature of the biogenic and fossil fractions (Fig. 3). As expected from visual inspection of Fig. 2 A and B, we retrieve a very high coefficient of determination,  $R^2$ , between  $C_{\text{xs}}$  and



**Fig. 2.** Time series of measured (A and B) and derived (C–E) quantities from three different sampling sites, as described in the main text. Orange is USC; Blue is GRA; Red is FUL. Black line and crosses are the MWO (background) smooth curve and data, respectively. Small symbols in A and B represent data with windspeeds less than  $1.5 \text{ m s}^{-1}$  or wind directions from over building rooftops.

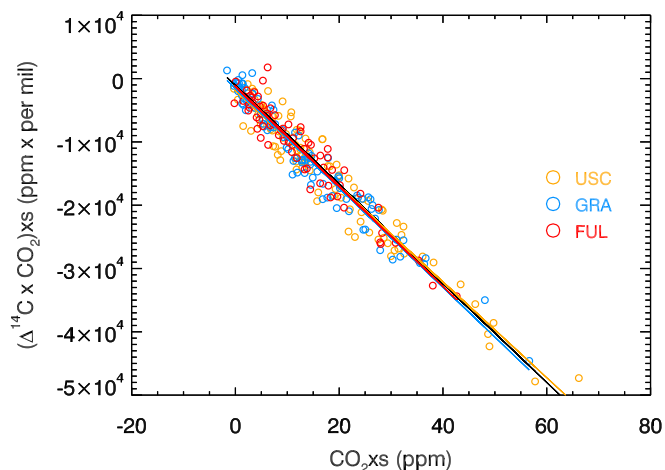
$(\Delta \times C)_{\text{xs}}$  of 0.94. However, the slope,  $\Delta_{\text{source}}$ , is  $-783 \pm 11\text{‰}$ . If  $C_{\text{xs}}$  were due solely to fossil fuel emissions, then  $\Delta_{\text{source}}$  would equal  $-1,000\text{‰}$  because fossil fuel contains zero  $^{14}\text{C}$ . To determine the fossil and biogenic fractions of  $C_{\text{xs}}$ ,  $f_{\text{ff}}$  and  $f_{\text{bio}}$  (corresponding to  $C_{\text{ff}}$  and  $C_{\text{bio}}$ , where  $C_{\text{bio}} = C_r + C_p$ ), we conduct a two end-member mixing analysis.  $\Delta_{\text{ff}} = -1,000\text{‰}$  and  $\Delta_{\text{bio}} = -16.5\text{‰}$  under the assumption that  $\Delta_{\text{bio}}$  is in equilibrium with the observed local atmosphere,  $\Delta_{\text{obs}}$ . This leads to estimated biogenic and fossil fractions of  $C_{\text{xs}}$  for L.A. of  $\sim 20\%$  and  $\sim 80\%$  (SI Appendix). Site-specific values of  $\Delta_{\text{source}}$  for GRA, USC, and FUL are  $-786 \pm 18\text{‰}$ ,  $-758 \pm 19\text{‰}$ , and  $-787 \pm 30\text{‰}$ , respectively, and overlap the slope from the combined dataset within uncertainties. Similarity between these sites was also observed previously in the statistical distributions of quasi-continuous measurements of  $\text{CO}_2$  mole fraction (24) and justifies pooling the data for the remainder of the analysis.

In order to isolate  $C_{\text{ff}}$  on a sample-by-sample basis, as in previous work (30), we set  $\Delta_p = \Delta_{\text{bg}}$  and combine Eqs. 1 and 2 (Fig. 2D):

$$C_{\text{ff}} = C_{\text{obs}}(\Delta_{\text{obs}} - \Delta_{\text{bg}})/(\Delta_{\text{ff}} - \Delta_{\text{bg}}) - C_r(\Delta_r - \Delta_{\text{bg}})/(\Delta_{\text{ff}} - \Delta_{\text{bg}}) \quad [3]$$

Eq. 3 shows that  $C_{\text{ff}}$  depends not just on the measured quantities, but also weakly on the biospheric disequilibrium term,  $-C_r(\Delta_r - \Delta_{\text{bg}})/(\Delta_{\text{ff}} - \Delta_{\text{bg}})$  (30, 43). To represent a likely maximum effect, we assume an isotopic disequilibrium ( $\Delta_r - \Delta_{\text{bg}}$ ) of  $+50\text{‰}$  (corresponding to an atmospheric growth rate of  $-5\text{‰ y}^{-1}$  and a biospheric residence time of 10 y) and a value of  $C_r$  of 5 ppm, which is about 25% larger than the mean winter (November–February) net biosphere mole fraction,  $C_{\text{bio}}$ , that is likely





**Fig. 3.** Isotope mixing analysis. The slopes of the fitted lines are isotope signatures of the flux-weighted sources, calculated as described in the main text. Colored lines represent the fits to data from each site, and the black line represents the fit to data from all sites. The slope of the black line is  $-783 \pm 11\%$  indicating a substantial contribution of biogenic sources to observed  $\text{CO}_2$  variability, as discussed in the text. Only data passing wind-speed and direction filtering criteria are shown and used in the regression. Linear regressions are calculated following the method of York et al. (2004) as described in *SI Appendix* (42).

dominated by  $C_r$ . This results in a disequilibrium correction of  $+0.25 \pm 0.00$  ppm (one-sigma SD), but the presence of the disequilibrium term has no impact on our conclusions. Derived  $C_{ff}$  averages  $13.2 \pm 9.4$  ppm with minimum and maximum values of  $-1.3$  and  $48.4$  ppm. (Note that a few instances of negative, nonphysical,  $C_{ff}$  are expected, given the one-sigma uncertainty of  $1.2$  ppm.) Although mean  $C_{ff}$  during the winter months (November–February;  $14.0 \pm 12.7$  ppm) is nearly the same as during the summer (May–September;  $13.2 \pm 6.9$  ppm), the variability is approximately twice as large in winter, mainly as a result of more instances of high  $C_{ff}$ . These likely result from increased atmospheric trapping of emissions in the boundary layer, as opposed to high emissions, because Hestia–L.A. (4) indicates that wintertime emissions are only 3% higher than those in summer. The fact that the annual SD of  $C_{ff}$  across all sites is  $9.4$  ppm, or 71% of its mean level, also suggests that atmospheric transport, rather than emissions, dominates the variability of observed  $C_{ff}$ . Such high variability in emissions is unlikely; large variations in atmospheric trapping of emissions due to variations in wind speed and planetary boundary layer (PBL) height are more likely.

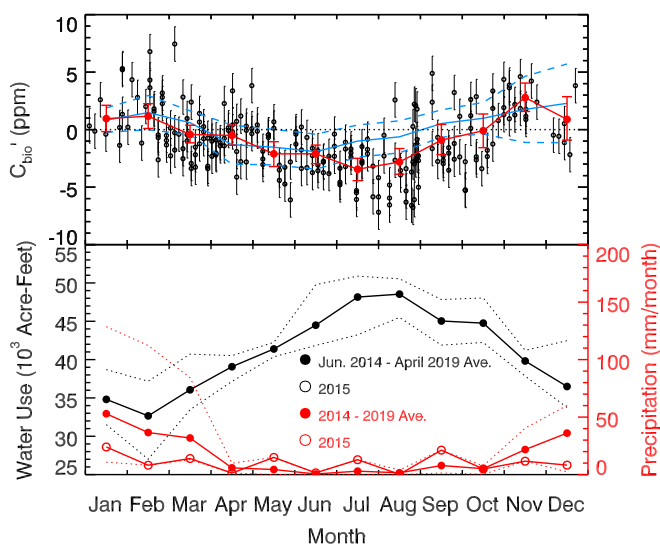
$C_{bio}$  (Fig. 2E) is calculated as the difference between  $C_{ff}$  and  $C_{xs}$  (Eq. 1). It shows an annual mean value of  $1.5 \pm 1.9$  ppm (mean and SD of monthly means), a mean wintertime enhancement of  $3.5 \pm 0.9$  ppm, and a much smaller summertime mean enhancement of  $-0.3 \pm 1.0$  ppm. Fifty-six percent of all summertime  $C_{bio}$  values are negative, indicating some degree of net  $\text{CO}_2$  uptake. In order to isolate the signal coming from the terrestrial biosphere, we estimate contributions to  $C_{bio}$  from biogenic sources such as biofuels and human respiration. According to the State of California’s Air Resources Board (CARB) emissions inventory, ethanol and biodiesel in the “on-road” sector are a leading source of biofuel emissions in the inventory ( $3.1 \text{ Tg C y}^{-1}$  statewide, or about 7% of total on-road), but other sectors such as “industrial” and “electricity production” ( $3.5$  and  $2.0 \text{ Tg C y}^{-1}$ , or 17% and 15%, respectively) also include significant biofuel use. For all  $\text{CO}_2$  emission sectors, we calculate biogenic:fossil emission ratios at the state level (where CARB inventory data are available) and apply these ratios to the

same emission sectors for the five Southern California counties covered by the Hestia–L.A. emissions inventory (*SI Appendix, Table S2*). Considering all sectors, we find a ratio of biogenic to fossil fluxes of 0.103. We estimate emissions for human respiration and excretion by applying a global relationship between human population and total human metabolic emissions (44) to populations for the five counties in Hestia–L.A. We find a ratio of human metabolic to fossil fluxes of 0.057 (*SI Appendix, Table S3*). Thus, the overall biogenic:fossil emission ratio for human metabolism and use of biofuels,  $R_{bio}$ , is 0.160. Applying this combined factor, we isolate the  $C_{bio}$  contributions coming from urban ecosystems, which we define as  $C_{bio}' = C_{bio} - R_{bio} \times C_{ff}$ . This results in an average annual  $C_{bio}'$  enhancement of  $-0.6 \pm 1.8$  and wintertime and summertime  $C_{bio}'$  mean values of  $1.5 \pm 0.9$  ppm and  $-2.3 \pm 1.0$  ppm, respectively. On average, individual  $C_{bio}'$  values are  $2.1$  ppm lower than  $C_{bio}$ . We test the sensitivity of  $C_{bio}'$  to the fuel-related portion of the overall correction factor by using an alternative biogenic:fossil ratio for fuel-related sectors of 0.050 derived from the Anthropogenic Carbon Emissions System version 2 (ACES v2) (45) (*SI Appendix*), resulting in an alternative  $R_{bio}$  of 0.107. The annual mean (based on monthly means) of  $C_{bio}'$  increases by  $0.7$  ppm, but the amplitude of the  $C_{bio}'$  seasonal cycle (November–January minus June–August; *SI Appendix*) remains unchanged at  $4.3$  ppm (*SI Appendix, Fig. S2*). This is not surprising, given that the correction factors are annual and that there is no significant seasonality in  $C_{ff}$ . Even in the case of uncorrected  $C_{bio}$ , the derived seasonal amplitude of  $4.1$  ppm is within 5% of the amplitude of the two  $C_{bio}'$  estimates. We also tested the sensitivity of the seasonal cycle amplitude of  $C_{bio}'$  to our choice of background site by using  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  measurements from Niwot Ridge, CO (NWR), which lies  $\sim 1,300$  km northwest of MWO and  $1,800$  m higher in elevation. Despite substantially different seasonal cycles of  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  at NWR and MWO (*SI Appendix, Fig. S3*), two thirds of the derived  $C_{bio}'$  amplitude is retained when using NWR as background. The relatively small sensitivity to rather different background values occurs because the local  $\text{CO}_2$  and  $\Delta^{14}\text{C}$  signals at GRA, USC, and FUL are so large.

The Mediterranean climate of Southern California is characterized by a winter rainy season that generally leads to a March/April maximum in carbon uptake for most unmanaged ecosystems (*SI Appendix, Fig. S4*). In contrast, the seasonality of derived  $C_{bio}'$  for the L.A. urban area resembles that of a temperate midlatitude ecosystem with maximum carbon uptake in the middle of the year (Fig. 4). In order to evaluate the possible impact of different moisture inputs on  $C_{bio}'$ , we compare the timing of  $C_{bio}'$  to locally representative records of precipitation and urban water use (Fig. 4). The precipitation maximum occurs in winter, as expected, but is associated with net biospheric emission rather than the uptake response characterizing most unmanaged ecosystems in the region (*SI Appendix, Fig. S4*). On the other hand, the timings of observed  $C_{bio}'$  and urban water use are well correlated (Fig. 4 and *SI Appendix, Fig. S5*), with peak water use and  $\text{CO}_2$  uptake in the summer months. This suggests that irrigation of urban turf (including lawns, golf courses, and parks) and other vegetation exerts a substantial control on urban  $C_{bio}'$ , overwhelming the influence of local precipitation. Although water use totals include consumption from industrial use, indoor use, and outdoor landscape irrigation, seasonal variation of total usage is most likely dominated by landscape irrigation (46). The potential contribution of urban vegetation to  $C_{bio}'$  is also supported by high-resolution land surface classification for the L.A. area based on the Airborne Visible InfraRed Imaging Spectrometer (AVIRIS) (47) showing a footprint weighted-mean tree and turf cover of 14% in the upwind fetch of our measurement sites (*SI Appendix, Fig. S6*). Analysis of remote sensing and aerial photography also indicate tree coverage of 21% and irrigated lawn coverage of 12% for the city of L.A. (48). Of the

available records of net ecosystem exchange (NEE) from unmanaged ecosystems, only that for the high-altitude (1,770 m.a.s.l.) Oak/Pine forest exhibits a seasonal cycle that is roughly in phase with the L.A.  $C_{bio}'$  signal (SI Appendix, Fig. S4). While the San Gabriel mountains that form the northern border of the L.A. Basin contain similar ecosystems, they are likely too distant from our sites to contribute significantly to observed  $C_{bio}'$ . Assuming that monthly mean NEE for the Oak/Pine site represents the NEE for all local forest cover above 1,500 m.a.s.l., we convolve sample footprints at each site with NEE maps and find the resulting simulated  $C_{bio}'$  amplitude at our measurement sites is not more than  $\sim 0.3$  ppm (SI Appendix, Fig. S7). Ultimately, sources such as urban trees and turf must be responsible for the vast majority of the observed  $C_{bio}'$  signal because unlike  $CO_2$  sources such as biofuel combustion and human metabolism, which can only be emissive, our observations also require seasonal carbon sinks.

As noted earlier, the L.A. region (located within the “South Coast District” of California) experienced “extreme drought” during our study period, with Palmer Drought Severity Index (PDSI) levels below  $-4$  in 2015 (SI Appendix, Fig. S8). The drought can also be seen in the deviation of local precipitation in 2015 from the 2014–2019 average and range (Fig. 4); in 2015, less than 60 mm of rain fell during the January through March rainy season. In order to assess the impact of the 2015 drought conditions on  $C_{bio}'$ , we analyze the CIT  $\Delta^{14}C$  record of Newman and coauthors (27), which has been extended to encompass



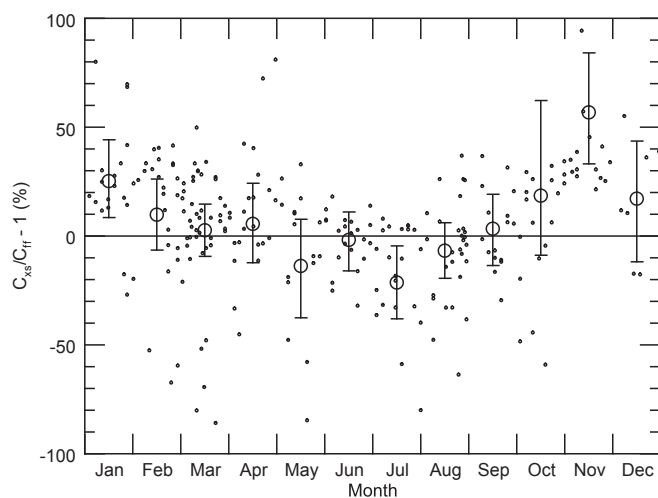
**Fig. 4.** (Top) The urban biospheric fraction of the excess  $CO_2$  signal ( $C_{bio}'$ ) shown for all samples (passing windspeed and wind direction screening) as open black circles with one-sigma random errors. Monthly mean  $C_{bio}'$  values are overplotted as filled red symbols. Red error bars represent 95% confidence intervals (CIs) for the means, calculated using a bootstrap method, as described in SI Appendix. The solid blue line shows the 2006–2015 mean monthly  $C_{bio}'$  from CIT (using LJO and BRW as background for  $CO_2$  and  $\Delta^{14}C$ , respectively), with the 10-y SDs shown in dashes. (Bottom) Water inputs to the study domain. Black symbols and lines represent total water usage for the area served by the L.A. Department of Water and Power as reported to the State of California Water Board ([https://www.waterboards.ca.gov/water\\_issues/programs/conservation\\_portal/conservation\\_reporting.html](https://www.waterboards.ca.gov/water_issues/programs/conservation_portal/conservation_reporting.html), accessed June 2019). Red symbols and lines represent monthly total precipitation from the Global Precipitation Climatology Project (GPCP v1.3) for the  $1^\circ \times 1^\circ$  degree grid cell containing the city of L.A. Red and black dashed lines represent the upper and lower bounds for the date ranges in the legend of either city water usage or precipitation and are referenced to the respective solid line with solid symbols. The lines with open symbols represent water usage or precipitation for 2015.

2006–2015, overlapping the period of our observations. The record consists of approximately twice-monthly  $\Delta^{14}C$  measurements made on air samples collected at about 10 m above ground level on the campus of the California Institute of Technology, located in the city of Pasadena in the eastern L.A. Basin. Following Newman et al. (27), we calculate  $C_{bio}$  using BRW for  $\Delta^{14}C$  background and Scripps Pier measurements at La Jolla, California (LJO) for  $CO_2$  background; to estimate  $C_{bio}'$  we use the default value of  $R_{bio}$  derived above. The CIT 2006–2015 mean seasonal cycle (Fig. 4 and SI Appendix, Fig. S9) is broadly similar to the 2015 seasonal cycle of  $C_{bio}'$  obtained from the L.A. megacity site data, except that the mean CIT results show maximum uptake in June rather than July. In 2015, CIT exhibits a  $C_{bio}'$  minimum in May. For 2015, the only full year for which MWO  $\Delta^{14}C$  data are currently available, we can recalculate CIT  $C_{bio}'$  using the nearer MWO site as background for  $CO_2$  and  $\Delta^{14}C$  instead of LJO and BRW, respectively. This results in a 2015 CIT  $C_{bio}'$  minimum in July, with a seasonality very similar to  $C_{bio}'$  of the L.A. megacity sites (SI Appendix, Fig. S10). This suggests that the timing of the 2006–2015 mean CIT  $C_{bio}'$  minimum could in fact be slightly later in the year, more in line with our 2015 observations. Irrespective of potential background artifacts, what is most notable about the 2006–2015 record of  $C_{bio}'$  at CIT is that 2015 does not stand out from the other 10 y (SI Appendix, Fig. S9). Although there were very dry (7 y with  $PDSI < -3$ ) and less dry (3 y with  $PDSI > -3$ ) years between 2006 and 2015, the difference in average  $C_{bio}'$  seasonal cycles between the two regimes is relatively small (SI Appendix, Fig. S9). The mean month of the  $C_{bio}'$  minimum for years with  $PDSI < -3$ ,  $PDSI > -3$ , and the 10-y mean all occur in June, and the mean amplitudes ( $7.7 \pm 3.1$  ppm for dry years and  $5.2 \pm 1.0$  ppm for “wet” years) are not statistically different ( $P > 0.10$ ). Neglecting the possibility that the CIT minima may be biased early due to misrepresentation of background, estimated maximum  $CO_2$  uptake signals are still much closer to peak water usage in July and August than to the period of peak climatological rainfall in January and February. This suggests that the influence of anthropogenic water inputs on urban biospheric  $CO_2$  exchange in L.A. is pervasive and not restricted to occasions of extreme drought such as occurred during our study period. Furthermore, while the 2015 L.A. megacity observations were associated with extreme drought, such conditions may increasingly represent the “new normal.” Between 2000 and 2019, 10 y have been “severe” ( $-4 < PDSI < -3$ ) or “extreme” droughts in the South Coast District (SI Appendix, Fig. S8).

Finally, we consider the observational bias in fossil fuel- $CO_2$  that would arise throughout the year by neglecting the role of biogenic  $CO_2$  and assuming that all of the  $CO_2$  enhancement observed in L.A. is derived from fossil fuel use. We show this effect in Fig. 5 by plotting the monthly relative bias,  $C_{xs}/C_{ff} - 1$ . For winter months (November–February) when  $C_{bio}$  is positive, the mean error is  $+27\%$ , and during summer (May–September), when  $C_{bio}$  tends to be negative, the bias is  $-7\%$ . The maximum and minimum monthly mean biases are  $+56 \pm 12\%$  (68% CI) and  $-21 \pm 8\%$ , occurring in November and July, respectively. These biases would not be detected without reliable methods to separate  $C_{bio}$  and  $C_{ff}$  (such as  $^{14}CO_2$  measurements), whether from surface measurements or remote sensing of the total atmospheric column. We note that relative bias ( $C_{xs}/C_{ff} - 1$ ) will be the same for observations of the total atmospheric column as for the PBL, if  $C_{ff}$  and  $C_{bio}$  are zero above the top of the PBL. This condition will be close to true when air parcels above the top of the PBL have minimal surface influence.

### Conclusions

We have shown the combination of atmospheric  $CO_2$  and  $\Delta^{14}C$  data in the L.A. megacity to be a powerful tracer for both the fossil and biogenic components of the total urban  $CO_2$  signal.



**Fig. 5.** Relative error induced by assuming that all of the  $C_{xs}$  signal is fossil (i.e.,  $C_{bio} = 0$ ). Small circles are values of  $C_{xs}/C_{ff} - 1$  for individual samples (passing the windspeed and wind direction threshold). Large circles are monthly means of those values; error bars are 95% CIs for medians calculated using bootstrap, with replacement, of individual values within a month, further accounting for individual uncertainties on  $C_{ff}/C_{xs} - 1$  values (as described in *SI Appendix*).

Overall, we find that  $\sim 20\%$  of local L.A.  $CO_2$  variability is biogenic. Our analysis further reveals that the amplitude of  $CO_2$  originating from the urban biosphere (4.3 ppm) is 33% of the annual mean fossil fuel contribution (13.0 ppm), a surprisingly large fraction for a naturally dry metropolitan area seemingly dominated by transportation and industrial emissions. The seasonality of observation-based  $C_{bio}$  from the drought year of 2015 is consistent with controls on urban NEE from urban water usage, and there is further evidence from the 10-y CIT  $C_{bio}$  record that urban water usage, more than rainfall, may drive the urban NEE response even in years when drought is less severe or absent. In the L.A. megacity, human activity appears to influence both fossil and vegetation  $CO_2$  fluxes—i.e., even the biospheric fluxes we observe are anthropogenic.

Accurately measuring the biospheric contribution to urban  $CO_2$  in L.A., and possibly other naturally arid urban areas in the United States and throughout the world, will be important in avoiding biases in estimated fossil fuel  $CO_2$  emissions that would otherwise result from measuring  $CO_2$  alone. The ability to separately track biogenic and fossil carbon fluxes will also become increasingly important to assess the impact of policies such as L.A.'s "Million Trees L.A." initiative (48) and to improve our understanding of the relationship between urban biospheric  $CO_2$  fluxes and natural and anthropogenic water inputs in the presence of a changing climate. Many current and future megacities with extensive tree cover are wetter than L.A. For tropical and

subtropical megacities such as Mumbai, India, and São Paulo, Brazil, this may result in annual average and monthly biospheric  $CO_2$  signals larger than we observe in this study. In the absence of constraints from reliable fossil fuel- $CO_2$  tracers such as  $\Delta^{14}C$ , undetected biospheric signals would result in potentially significant observational biases in fossil fuel- $CO_2$  emissions that could vary from year to year, hampering the ability to accurately quantify urban fossil fuel- $CO_2$  emissions trends using top-down methods.  $\Delta^{14}C$  and  $CO_2$  measurements from a variety of temperate midlatitude cities such as Indianapolis, Heidelberg, Paris, and Krakow (29, 31, 34, 49) also show that, even during winter, neglecting  $C_{bio}$  may result in biased estimates of atmospheric concentrations and emissions of fossil fuel- $CO_2$ .

It may not be feasible to deploy  $\Delta^{14}C$  measurements in all large cities to the extent we have in L.A. and other urban areas such as Indianapolis (34). However, periodic  $\Delta^{14}C$  measurements will be necessary to track the interannual variability and trends of  $C_{ff}$  and  $C_{bio}$  resulting from growing urban populations, changing fuel types and usage, emissions reduction efforts, and urban greening campaigns, as well as climate. One effective monitoring strategy that greatly leverages relatively costly  $^{14}C$  measurements may be to "calibrate" other anthropogenic tracers such as CO against  $^{14}C$ -based  $C_{ff}$  (33, 35). Since CO can be measured continuously and at lower cost than  $^{14}C$ , it can be used together with a limited number of  $^{14}C$  measurements to provide an accurate and quasi-continuous proxy for  $C_{ff}$ . Because constraining  $C_{ff}$  also constrains  $C_{bio}$ , such an observing strategy could be used to evaluate and improve models of the urban biosphere, such as the Urban Vegetation Photosynthesis and Respiration Model (VPRM) (23). Measurements of  $CO_2$ ,  $\Delta^{14}C$ , and CO (or other proxies) have great potential to optimize both fossil and biospheric fluxes using urban-scale inversions and can thus improve the accuracy of both top-down and bottom-up approaches meant to assess the efficacy of urban emissions mitigation efforts.

**Data Availability.** All study data are included in the article and *SI Appendix*.

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- G. A. Folberth, T. M. Butler, W. J. Collins, S. T. Rumbold, Megacities and climate change—A brief overview. *Environ. Pollut.* **203**, 235–242 (2015).
- United Nations, *World Urbanization Prospects: The 2018 Revision (ST/ESA/SER/A/420)*, Population Division of the Department of Economic and Social Affairs, Ed. (United Nations, New York, 2019).
- R. M. Duren, C. E. Miller, Measuring the carbon emissions of megacities. *Nat. Clim. Change* **2**, 560–562 (2012).
- K. R. Gurney et al., The Hestia fossil fuel  $CO_2$  emissions data product for the Los Angeles megacity (Hestia-LA). *Earth Syst. Sci. Data* **11**, 1309–1335 (2019).
- G. Janssens-Maenhout et al., *Fossil  $CO_2$  and GHG Emissions of all World Countries*, (Publications Office of the European Union, Luxembourg, 2017).
- S. Basu, J. B. Miller, S. Lehman, Separation of biospheric and fossil fuel fluxes of  $CO_2$  by atmospheric inversion of  $CO_2$  and  $^{14}CO_2$  measurements: Observation System Simulations. *Atmos. Chem. Phys.* **16**, 5665–5683 (2016).
- S. Feng et al., Los Angeles megacity: A high-resolution land-atmosphere modelling system for urban  $CO_2$  emissions. *Atmos. Chem. Phys.* **16**, 9019–9045 (2016).
- D. F. Baker et al., TransCom 3 inversion intercomparison: Impact of transport model errors on the interannual variability of regional  $CO_2$  fluxes, 1988–2003. *Global Biogeochem. Cycles* **20**, GB1002 (2006).
- C. Le Quéré et al., Temporary reduction in daily global  $CO_2$  emissions during the COVID-19 forced confinement. *Nat. Clim. Change* **10**, 647–653 (2020).
- R. M. Duren et al., California's methane super-emitters. *Nature* **575**, 180–184 (2019).
- K. R. Gurney et al., Sensitivity of atmospheric  $CO_2$  inversions to seasonal and inter-annual variations in fossil fuel emissions. *J. Geophys. Res.* **110**, D10308 (2005).
- Y. P. Shiga, A. M. Michalak, S. M. Gourdji, K. L. Mueller, V. Yadav, Detecting fossil fuel emissions patterns from subcontinental regions using North American in situ  $CO_2$  measurements. *Geophys. Res. Lett.* **41**, 4381–4388 (2014).
- S. Basu et al., Estimating US fossil fuel  $CO_2$  emissions from measurements of  $^{14}C$  in atmospheric  $CO_2$ . *Proc. Natl. Acad. Sci. U.S.A.* **117**, 13300–13307 (2020).
- E. A. Kort, C. Frankenberg, C. E. Miller, T. Oda, Space-based observations of megacity carbon dioxide. *Geophys. Res. Lett.* **39**, L17806 (2012).



15. J. Hakkarainen, I. Ialongo, J. Tamminen, Direct space-based observations of anthropogenic CO<sub>2</sub> emission areas from OCO-2. *Geophys. Res. Lett.* **43**, 11400–11406 (2016).
16. D. Wunch, P. O. Wennberg, G. C. Toon, G. Keppel-Aleks, Y. G. Yavin, Emissions of greenhouse gases from a North American megacity. *Geophys. Res. Lett.* **36**, L15810 (2009).
17. T. Lauvaux *et al.*, High-resolution atmospheric inversion of urban CO<sub>2</sub> emissions during the dormant season of the Indianapolis Flux Experiment (INFLUX). *J. Geophys. Res. Atmos.* **121**, 5213–5236 (2016).
18. J. K. Hedelius *et al.*, Southern California megacity CO<sub>2</sub>, CH<sub>4</sub>, and CO flux estimates using ground- and space-based remote sensing and a Lagrangian model. *Atmos. Chem. Phys.* **18**, 16271–16291 (2018).
19. D. Wu, J. C. Lin, T. Oda, E. A. Kort, Space-based quantification of per capita CO<sub>2</sub> emissions from cities. *Environ. Res. Lett.* **15**, 035004 (2020).
20. K. McKain *et al.*, Assessment of ground-based atmospheric observations for verification of greenhouse gas emissions from an urban region. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 8423–8428 (2012).
21. J. Stauffer *et al.*, The first 1-year-long estimate of the Paris region fossil fuel CO<sub>2</sub> emissions based on atmospheric inversion. *Atmos. Chem. Phys.* **16**, 14703–14726 (2016).
22. M. Sargent *et al.*, Anthropogenic and biogenic CO<sub>2</sub> fluxes in the Boston urban region. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 7491–7496 (2018).
23. B. S. Hardiman *et al.*, Accounting for urban biogenic fluxes in regional carbon budgets. *Sci. Total Environ.* **592**, 366–372 (2017).
24. K. R. Verhulst *et al.*, Carbon dioxide and methane measurements from the Los Angeles Megacity Carbon Project—Part 1: Calibration, urban enhancements, and uncertainty estimates. *Atmos. Chem. Phys.* **17**, 8313–8341 (2017).
25. C. Park *et al.*, CO<sub>2</sub> transport, variability, and budget over the Southern California Air Basin using the high-resolution WRF-VPRM model during the CalNex 2010 campaign. *J. Appl. Meteorol. Climatol.* **57**, 1337–1352 (2018).
26. S. Newman *et al.*, Diurnal tracking of anthropogenic CO<sub>2</sub> emissions in the Los Angeles Basin megacity during spring 2010. *Atmos. Chem. Phys.* **13**, 4359–4372 (2013).
27. S. Newman *et al.*, Toward consistency between trends in bottom-up CO<sub>2</sub> emissions and top-down atmospheric measurements in the Los Angeles megacity. *Atmos. Chem. Phys.* **16**, 3843–3863 (2016).
28. J. Brioude *et al.*, Top-down estimate of surface flux in the Los Angeles Basin using a mesoscale inverse modeling technique: Assessing anthropogenic emissions of CO, NO<sub>x</sub> and CO<sub>2</sub> and their impacts. *Atmos. Chem. Phys.* **13**, 3661–3677 (2013).
29. I. Levin, B. Kromer, M. Schmidt, H. Sartorius, A novel approach for independent budgeting of fossil fuel CO<sub>2</sub> over Europe by <sup>14</sup>CO<sub>2</sub> observations. *Geophys. Res. Lett.* **30**, 2194 (2003).
30. J. C. Turnbull *et al.*, Comparison of <sup>14</sup>CO<sub>2</sub>, CO, and SF<sub>6</sub> as tracers for recently added fossil fuel CO<sub>2</sub> in the atmosphere and implications for biological CO<sub>2</sub> exchange. *Geophys. Res. Lett.* **33**, L01817 (2006).
31. M. Lopez *et al.*, CO, NO<sub>x</sub> and <sup>13</sup>CO<sub>2</sub> as tracers for fossil fuel CO<sub>2</sub>: Results from a pilot study in Paris during winter 2010. *Atmos. Chem. Phys.* **13**, 7343–7358 (2013).
32. I. Levin, S. Hammer, E. Eichelmann, F. R. Vogel, Verification of greenhouse gas emission reductions: The prospect of atmospheric monitoring in polluted areas. *Philos. Trans. A Math. Phys. Eng. Sci.* **369**, 1906–1924 (2011).
33. F. R. Vogel, S. Hammer, A. Steinhof, B. Kromer, I. Levin, Implication of weekly and diurnal <sup>14</sup>C calibration on hourly estimates of CO<sub>2</sub>-based fossil fuel CO<sub>2</sub> at a moderately polluted site in southwestern Germany. *Tellus B Chem. Phys. Meteorol.* **62**, 512–520 (2010).
34. J. C. Turnbull *et al.*, Toward quantification and source sector identification of fossil fuel CO<sub>2</sub> emissions from an urban area: Results from the INFLUX experiment. *J. Geophys. Res. Atmos.* **120**, 292–312 (2015).
35. J. C. Turnbull *et al.*, Assessment of fossil fuel carbon dioxide and other anthropogenic trace gas emissions from airborne measurements over Sacramento, California in spring 2009. *Atmos. Chem. Phys.* **11**, 705–721 (2011).
36. C. Sweeney *et al.*, Seasonal climatology of CO<sub>2</sub> across North America from aircraft measurements in the NOAA/ESRL Global Greenhouse Gas Reference Network. *J. Geophys. Res. Atmos.* **120**, 5155–5190 (2015).
37. J. C. Turnbull *et al.*, A new high precision <sup>14</sup>CO<sub>2</sub> time series for North American continental air. *J. Geophys. Res.* **112**, D11310 (2007).
38. S. J. Lehman *et al.*, Allocation of terrestrial carbon sources using <sup>14</sup>CO<sub>2</sub>: Methods, measurement, and modeling. *Radiocarbon* **55**, 1484–1495 (2013).
39. V. Yadav *et al.*, Spatio-temporally resolved methane fluxes from the Los Angeles megacity. *J. Geophys. Res. Atmos.* **124**, 5131–5148 (2019).
40. K. A. Masarie, P. P. Tans, Extension and integration of atmospheric carbon-dioxide data into a globally consistent measurement record. *J. Geophys. Res.* **100**, 11593–11610 (1995).
41. J. B. Miller, P. P. Tans, Calculating isotopic fractionation from atmospheric measurements at various scales. *Tellus B Chem. Phys. Meteorol.* **55**, 207–214 (2003).
42. D. York, N. M. Evensen, M. L. Martinez, J. De Basabe Delgado, Unified equations for the slope, intercept, and standard errors of the best straight line. *Amer. J. Phys.* **72**, 367–375 (2004).
43. J. B. Miller *et al.*, Linking emissions of fossil fuel CO<sub>2</sub> and other anthropogenic trace gases using atmospheric <sup>14</sup>CO<sub>2</sub>. *J. Geophys. Res.* **117**, D08302 (2012).
44. Y. T. Prairie, C. M. Duarte, Direct and indirect metabolic CO<sub>2</sub> release by humanity. *Biogeosciences* **4**, 215–217 (2007).
45. C. K. Gately, L. R. Hutyrá, Large uncertainties in urban-scale carbon emissions. *J. Geophys. Res. Atmos.* **122**, 11242–11260 (2017).
46. C. Mini, T. S. Hogue, S. Pincetl, Estimation of residential outdoor water use in Los Angeles, California. *Landscapes Urban Plann.* **127**, 124–135 (2014).
47. E. B. Wetherley, J. P. McFadden, D. A. Roberts, Megacity-scale analysis of urban vegetation temperatures. *Remote Sens. Environ.* **213**, 18–33 (2018).
48. E. G. McPherson, J. R. Simpson, Q. Xiao, C. Wu, Million trees Los Angeles canopy cover and benefit assessment. *Landscapes Urban Plann.* **99**, 40–50 (2011).
49. M. Zimnoch *et al.*, Partitioning of atmospheric carbon dioxide over Central Europe: Insights from combined measurements of CO<sub>2</sub> mixing ratios and their carbon isotope composition. *Isotopes Environ. Health Stud.* **48**, 421–433 (2012).