Toward consistency between trends in bottom-up CO_2 emissions and top-down atmospheric measurements in the Los Angeles megacity

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Abstract

Large urban emissions of greenhouse gases result in large atmospheric enhancements relative to background that are easily measured. Using CO_2 mole fractions and $\Delta^{14}C$ and $\delta^{13}C$ values of CO_2 in the Los Angeles megacity observed in inland Pasadena (2006-2013) and coastal Palos Verdes peninsula (autumn 2009-2013), we have determined time series for CO_2 contributions from fossil fuel combustion (C_{ff}) for both sites and broken those down into contributions from petroleum/gasoline and natural gas burning for Pasadena. We find a 10 % reduction in Pasadena C_{ff} during the Great Recession of 2008-2010, which is consistent with the bottom-up inventory determined by the California Air Resources Board. The isotopic variations and total atmospheric CO_2 from our observations are used to infer seasonality of natural gas and petroleum combustion. The trend of CO_2 contributions to the atmosphere from natural gas combustion is out of phase with the seasonal cycle of total natural gas combustion seasonal patterns in bottom-up inventories but is consistent with the seasonality of natural gas usage by the area's electricity generating power plants. For petroleum, the inferred seasonality of CO_2 contributions from burning petroleum is delayed by several months relative to usage indicated by statewide gasoline taxes. Using the high-resolution Hestia-LA data product to compare C_{ff} from parts of the basin sampled by winds at different times of year, we find that variations in observed fossil fuel CO_2 reflect seasonal variations in wind direction. The seasonality of the local CO_2 excess from fossil fuel combustion along the coast, on Palos Verdes peninsula, is higher in fall and winter than spring and summer, almost completely out of phase with that from Pasadena, also because of the annual variations of winds in the region. Variations in fossil fuel CO_2

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signals are consistent with sampling the bottom-up Hestia-LA fossil CO_2 emissions product for sub-city source regions in the LA megacity domain when wind directions are considered.

1 Introduction

Carbon dioxide is the most important greenhouse gas (GHG) contributing to current global warming, contributing 64 % of the total radiative forcing, according to the IPCC AR5 report (IPCC, 2013) and comprising 82 % of GHG emissions (NRC, 2010). The global average mole fraction of CO_2 has increased approximately 40 % since pre-industrial times due to anthropogenic emissions (IPCC, 2013). Since the proportion of the world's emissions from megacities (urban regions with more than 10 million inhabitants) is out of proportion with their small surface area (EDGAR, 2009; IEA, 2008), quantifying C_{ff} is essential if we are to work aggressively toward their reduction (Duren and Miller, 2012). As a consequence of global warming mitigation, reducing C_{ff} could reduce air pollution mortality, which is correlated with increased CO_2 levels (Jacobson, 2008).

Identifying the sources of emissions is a major first step in understanding and mitigating anthropogenic contributions. In cities, especially in megacities, these CO_2 sources often dominate over the normally predominant natural source of the biosphere, at least during certain seasons (e.g., Pataki et al., 2003; Widory and Javoy, 2003; Newman et al., 2013; 2008; Lopez et al., 2013; Turnbull et al., 2011; 2015; Vardag et al., 2015). The most common method of inventorying CO_2 emissions from human activities is through bottom-up reporting by governmental agencies, following IPCC methods (IPCC, 2013). Uncertainties in these methods range from 3-5 % to greater than 50 % (Andres et al., 2012). A more recent, scientifically-based bottom-up approach has been pioneered through the Vulcan and Hestia projects (Gurney et al., 2009; Gurney et al., 2012). These efforts combine multiple streams of data such as air pollution reporting, demographics,

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property tax data, and traffic monitoring, to arrive at what is proving to be a much more accurate and space/time detailed estimate of fossil fuel CO_2 emissions. The Vulcan Project accomplished fossil fuel CO_2 emission estimation for the whole US at spatial scales of 10 km every hour of the year 2002, with updated years expected by the end of 2015. Hestia is specifically focused on the urban domain and has accomplished estimation down to the individual building and street segment scale for four cities (Indianapolis, IN; Salt Lake City, UT; Los Angeles basin, CA; Phoenix, AZ) with work ongoing in Baltimore, MD (Gurney et al., 2012, Patarasuk et al., in prep.; Rao et al., 2015). Both of these detailed data products are available for selected cities in the United States, facilitating top-down emissions quantification through long-term ambient air monitoring (Duren and Miller, 2012; Gurney et al., 2015). Trends in C_{ff} must be monitored precisely in order to evaluate progress towards mandated emission reductions. As an example, the California Global Warming Solutions Act of 2006 (Assembly Bill 32) requires reduction of greenhouse gas emissions to 1990 levels by 2020, a reduction of about 15 %. Indeed, now is the time to document the current level of emissions, as governments begin to implement strategies to reduce emissions (e.g., California's Cap-and-Trade Program and Low Carbon Fuel Standards) and want to be able to assess their efficacy.

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Within megacities, atmospheric CO_2 concentrations are often highly elevated relative to the regional background due to locally emitted carbon dioxide. This excess can be analyzed for its isotopic composition to help attribute the local emissions to specific processes. Radiocarbon (^{14}C) analyses give quantitative information as to the proportions of CO_2 resulting from combustion of ancient sources of carbon (fossil fuels)

relative to sources incorporating modern carbon, such as the biosphere (e.g., Levin et al., 2003; Levin and Roedenbeck, 2008; Turnbull et al., 2009), because of its short half-life of 5730 years. The stable isotopes of carbon can be used to separate sources with differing values, such as natural gas and petroleum combustion, with the $^{13}C/^{12}C$ ratio of natural gas typically being lower than that of petroleum (e.g., Keeling, 1961; 1958; Newman et al., 2008; 2013; Pataki et al., 2003; Widory and Javoy, 2003; Djuricin et al., 2010; Moore and Jacobson, 2015), although there can be overlap between petroleum combustion and biological respiration. Therefore, if we know the biosphere's contribution from the fossil fuel CO_2 contribution derived from $\Delta^{14}C$ and the total CO_2 enhancement over background, we can distinguish all three sources (biosphere, petroleum combustion, and natural gas combustion) provided that there are large variations, such as in urban regions.

Here we report the use of ^{14}C combined with $\delta^{13}C$ in flask samples to disaggregate the local emissions of CO_2 in the Los Angeles (LA) basin into biosphere, natural gas, and petroleum combustion sources. We investigate the annual patterns and trends for 2006-2013 in these components and compare them to global background and to bottom-up inventories generated by government agencies and scientific colleagues. In particular, we test the method against the changes in C_{ff} observed during and after the Great Recession of 2008-2010 in LA.

The sampling, analytical methods, and calculations are described in section 2. Section 3 discusses the results with regard to spatial and temporal variations and comparison with bottom-up inventories and the detailed data product Hestia-LA. Overall conclusions are presented in section 4.

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2 Data and analysis

2.1 Locations

Samples were collected at two locations in the Los Angeles basin: on the campus of the California Institute of Technology (Caltech) in Pasadena, CA (34°8'12"N, 118°7'39"W, (240 ± 5) m above sea level), and on Palos Verdes peninsula overlooking the Pacific Ocean and Santa Catalina Island to the south (33°44.7'N, 118°20.9'W, 330 m above sea level) (Fig.1). Pasadena is located in the San Gabriel valley, approximately 14 km NE of downtown Los Angeles and 40 km from the coast. Prevailing winds from the SW bring marine air from the ocean during daytime hours, as the planetary boundary layer deepens during heating of the land. During these periods of prevailing south to west winds, the Palos Verdes site is a credible background site. Since the marine air picks up emissions from the basin during its transit inland, Pasadena is a good receptor site for LA emissions. The San Gabriel Mountains just 5 km to the north act as a barrier until midday, when upslope flow and the rising temperature inversion layer allow venting over the mountains (Lu and Turco, 1994; 1995).

2.2 Samples

Air samples were collected into evacuated one-liter Pyrex flasks through Synflex 1300 tubing after passing through $Mg(ClO_4)_2$ to dry the samples. In Pasadena, samples were collected on alternate afternoons at 1400 Pacific Standard Time (PST) using an autosampler, whereas at the Palos Verdes site samples were collected manually once a week (on weekend days) between 1100 and 1600 PST, and typically near 1400 PST. The

mid-afternoon sampling time was chosen because this is when the planetary boundary layer tends to be the deepest and most well mixed during the day. The sampling path at each location was purged with ambient air before collection.

CO_2 was extracted from the air samples cryogenically, following the methods described in Newman et al. (2008), with the amount of CO_2 determined manometrically. Then the $\delta^{13}C$ was determined relative to the Vienna PDB (VPDB) standard (Coplen, 1996) by dual-inlet isotope ratio mass spectrometry (Thermo-Finnigan MAT 252; Bremen, Germany) on each individual sample. After this analysis, the CO_2 was frozen into a cold finger and combined with 3-7 other individual samples to create a composite sample characterizing mid-afternoon air over a two-week (Pasadena) or month (Palos Verdes) time period for $\Delta^{14}C$ analysis. This differs from the sampling protocol of Affek et al. (2006), who collected on average two 5-liter samples per month, analyzed each sample separately, and then averaged the results to produce monthly average $\Delta^{14}C$ values for 2004-2005. We found that by combining smaller samples collected more frequently (alternate days in Pasadena) our results were less scattered than in the previous report and therefore give interpretable seasonal variations. $\Delta^{14}C$ was analyzed by accelerator mass spectrometer at the Keck-CCAMS facility at the University of California, Irvine, using the methods described in Newman et al. (2013) and Xu et al. (2007). Analyses of air from standard tanks calibrated by NOAA (National Oceanic and Atmospheric Administration) gave errors for CO_2 mole fractions averaging of ± 1.4 ppm (1 ppm = 1 μmol mol^{-1}) (n = 44) and $\delta^{13}C$ of ± 0.15 ‰ (n = 30), including extraction, manometry, and mass spectrometry. Although the uncertainties in the CO_2 mole fractions is much higher than by spectroscopic techniques, it contributes less than half of the total

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uncertainty in C_{ff}, which is dominated by the $\Delta^{14}C$ average error of 2 ‰, based on long-term reproducibility of secondary standards (Xu et al., 2007; Xu et al., 2010; Graven et al, 2013; Miller et al., 2013).

2.3 Calculations

A major goal of this study is the attribution of the sources of the C_{ff} observed. A schematic figure of the flow of data used to calculate the portion of the total CO_2 that is due to biosphere respiration (bio) and fossil fuel (ff) combustion, including burning of petroleum (pet) and natural gas (ng), is shown in Fig. 2. Mole fractions of CO_2 measured at the two sites and a background site in La Jolla, CA, were used to calculate the CO_2 excess (xs) over background (bg). The contributions of fossil fuel combustion and the biosphere to the excess were determined from radiocarbon measurements, and the fossil fuel component was further broken down into petroleum and natural gas using $\delta^{13}C$ of the CO_2. Details are described below.

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2.3.1 Total CO_2 emissions and background CO_2 mole fraction

The CO_2 excess caused by local emissions at the two sites was calculated by subtracting an estimate of the background CO_2 mole fraction derived from La Jolla monthly values (Keeling et al., 2005; Figs. 3 and 4). Flask sampling at La Jolla is done so as to minimize the influence of local CO_2 sources by sampling during periods that simultaneously satisfy three criteria: low variability in CO_2 concentration for periods of 3 hours or more, wind speed of 2.6 m s^{-1} or more from a narrow southwesterly to westerly sector, and high visibility. That these methods successfully minimize influences

of local fossil-fuel emissions is indicated by the consistency of the annual radiocarbon concentrations at La Jolla compared to clean stations both to the north and south in the Northern Hemisphere (Graven, 2012). In this paper, therefore, the La Jolla data presented are screened background data. The La Jolla data were interpolated to determine the appropriate value for the midpoint of the range of collection dates included in each $\Delta^{14}C$ sample, using the algorithm from Thoning et al. (1989), with two harmonic terms, three polynomial terms, and the smoothed residuals of the long term trend (cutoff of 667 days).

2.3.2 CO_2 from fossil fuels, based on $\Delta^{14}C$

Mass balance calculations were used to calculate the relative contributions of background air, biosphere respiration and photosynthesis, and fossil fuel combustion (including natural gas and oil) to the CO_2 collected at the two sites. The following equations quantitatively separate the background air, biosphere, and fossil fuel combustion contributions to the locally measured atmospheric CO_2 using $\Delta^{14}C$ (e.g., Levin et al., 2003; Miller et al., 2012; Pataki et al., 2003; Turnbull et al., 2006; Fig. 4):

$$C_{obs} = C_{bg} + C_{ff} + C_r + C_p \quad (1)$$

$$\Delta_{obs}C_{obs} = \Delta_{bg}C_{bg} + \Delta_{ff}C_{ff} + \Delta_r C_r + \Delta_p C_p \quad (2)$$

where subscripts obs, bg, ff, r and p indicate observed, background, fossil fuels, respiration, and photosynthesis, respectively, C indicates CO_2 mole fraction in ppm, and Δ indicates $\Delta^{14}C$ in ‰. We assume that Δ_p is equivalent to Δ_{bg}, since natural fractionation during uptake is corrected in the $\Delta^{14}C$ measurement and therefore substitute

Δ_{bg} for Δ_p in Eq. (2). Then, after solving Eq. (1) for C_p and substituting this for C_p in Eq. (2), we solve Eq. (2) for C_{ff}, resulting in the following expression for C_{ff}:

$$C_{ff} = \frac{C_{obs}(\Delta_{obs}-\Delta_{bg})}{\Delta_{ff}-\Delta_{bg}} - \frac{C_r(\Delta_r-\Delta_{bg})}{\Delta_{ff}-\Delta_{bg}} \quad (3)$$

The value of Δ_{ff} is -1000 ‰, since fossil fuels contain no ^{14}C because they have been removed from the source of this short-lived radionuclide for millions of years.

We use the record from Pt. Barrow, AK (Xiaomei Xu, unpublished data) for the concurrent background $\Delta^{14}C$ values (Δ_{bg}), because this is the most complete record available for the entire time period of this study. The background $\Delta^{14}C$ record at Pt. Barrow, AK is obtained through the UCI/NOAA ESRL (Earth System Research Laboratory) flask network program that collects whole air samples using 6-L, 1-valve stainless steel canisters (Silco Can, Restek Co.) that have been pre-evacuated at UCI. The canisters are pressurized to ~2 atm using an oil-free pump. Two biweekly samples were collected before 2008, and one weekly afterwards. For the period from 17 June 2005 to 17 March 2006, some duplicate samples were collected using 32-L, 1-valve stainless steel canisters. Subsamples were then taken from these samples for ^{14}C analysis. CO_2 is extracted cryogenically at UCI then converted to graphite by the sealed tube zinc reduction method (Xu et al. 2007). Each sample is ~2.7 mg C in size. Analysis of $\Delta^{14}C$ is performed at the W M Keck AMS facility at UCI with total measurement uncertainty of ±1.3–2.4‰. Mass dependent fractionation is corrected for using "on-line" $\delta^{13}C$ measurements during AMS analysis, which accounts for fractionation that occurred during graphitization and inside the AMS. Comparison was made of 22 common sample dates spanning 5 yr, of measured $\Delta^{14}C$ from Barrow between the UCI and the Scripps Institution of Oceanography's CO_2 Program. It shows differences in measured $\Delta^{14}C$ are

consistent with the reported uncertainties and there is no significant bias between the programs (Graven et al., 2013). Another inter-comparison is that of AMS-based atmospheric $^{14}CO_2$ measurements organized by the NOAA Earth System Research Laboratory, Boulder, Colorado. The UCI lab is one the three groups having inter-laboratory comparability within 1‰ for ambient level $^{14}CO_2$ (Miller et al. 2013). Comparison of the Pt. Barrow data with those from La Jolla (Graven et al., 2012; Fig. 5) shows good agreement for 2004-2007, when the two data sets overlap. Comparing the calculated values for C_{ff} from these two backgrounds and propagating through the time series calculations (Section 3.4) results in a difference of approximately 1 % of the signal we are measuring. We calculate C_{bio} (the sum of C_r and C_p) from Eq. (1), using the calculated values of C_{ff} and the independent estimates of C_{bg} from the La Jolla data, so that we understand the contribution of the biosphere to total local emissions.

The nuclear power plant contribution, the only other source of ^{14}C, is small on the west coast of the U.S. (Graven and Gruber, 2011) and therefore is ignored.

Following Turnbull et al. (2006) and Miller et al. (2012), the respiration terms in the equations above are assumed to reflect contributions due to heterotrophic respiration. Thus, the second term in Eq. (3) is small in magnitude and is due to heterotrophic respiration, through which microbes respire CO_2 that was from carbon previously incorporated through photosynthesis. This term takes into account the isotopic disequilibrium due to the significant time delay between photosynthetic incorporation and respiration, assumed to be 10 years on average (Miller et al., 2012). The magnitude of this correction for our urban Pasadena site is different relative to sites with smaller anthropogenic CO_2 signals, since the CO_2 photosynthesized into the plant a decade ago

283 was not close to the background air composition of that time but was the local, "polluted"
284 air. The Δ_r in Eq. (3) for each sample was calculated by extrapolating the Pasadena trend
285 back 10 years. Because of the mild climate in southern California, we used a constant
286 value of C_r = 5 ppm, the same value used for summer by Turnbull et al. (2006). This
287 should be taken as an upper limit for this urban region. The range of the correction for
288 the second term in Eq. (3), including the sign, was -0.06 – -0.11 ppm, generally smaller
289 relative to regions where the biosphere contribution C_r is large (Miller et al., 2012;
290 Turnbull et al., 2006). For the data from the Palos Verdes site, we calculated the
291 heterotrophic correction term using values of Δ_r calculated by extrapolating the Pt.
292 Barrow background trend back 10 years and used a constant value of C_r = 5 ppm, because
293 of the mild climate. The correction term for the Palos Verdes data ranged from 0.20 –
294 0.24 ppm. The small correction for heterotrophic respiration does not affect any of our
295 conclusions.
296 In California, there is an added complication when attributing CO_2 emissions to
297 fossil fuels using $\Delta^{14}C$. Since 2004, 10 % ethanol has been added to gasoline. The
298 ethanol contains modern, not fossil, carbon. For gasoline with 10 % ethanol, 6.7 % of the
299 CO_2 emitted during combustion is from the modern ethanol (EIA, 2015). A correction
300 for this is made, as discussed in section 2.3.3 below.
301
302 **2.3.3 $\delta^{13}C$ of CO_2**
303 Plots involving the mole fractions and $\delta^{13}C$ can be used to determine $\delta^{13}C$ of the
304 local contribution to the observed CO_2 (Fig. 3). Here we use the Miller-Tans approach
305 (Miller-Tans approach; MT; Miller and Tans, 2003) for this purpose, since it allows for

variations in background composition and we observe a widening difference between the data for $\delta^{13}C$ in Pasadena and the La Jolla background record in recent years (Fig. 3e). The following mass balance equations are used in this analysis:

$$C_{obs} = C_{bg} + C_{src} \quad (4)$$

$$\delta_{obs} * C_{obs} = \delta_{bg} * C_{bg} + \delta_{src} * C_{src} \quad (5)$$

to give

$$\delta_{obs} * C_{obs} - \delta_{bg} * C_{bg} = \delta_{src}(C_{obs} - C_{bg}) \quad (6)$$

(Miller and Tans, 2003), where the subscript src represents the local source of CO_2 emissions, δ represents $\delta^{13}C$, and the appropriate background values are included for each sample. Using this formulation (Eq. 6), the slope of the correlation (MT slope) gives the $\delta^{13}C$ of this local source. For this analysis, we calculated the MT slopes for each month and then determined the seasonal averages, averaging December-January-February as winter, March-April-May as spring, June-July-August as summer, and September-October-November as autumn. Seven individual samples, over the eight-year sampling period in Pasadena, were excluded since they fell more than three times the standard error from their linear regression best-fit lines. The monthly MT plots for 2011 are shown in Fig. A1, as examples. The very high correlation coefficients (R = 0.952 – 0.999) suggest that δ_{src} remains constant on time scales of a month. We assume that this is also the case for the isotopic compositions of petroleum and natural gas combustion, that we describe below.

We use the results from the $^{14}CO_2$ calculations for the fraction of C_{xs} from the biosphere ($F_{bio} = 1 - F_{ff}$) together with the MT slopes to attribute the CO_2 derived from

petroleum and natural gas combustion (C_{pet} and C_{ng}) by mass balance, first by calculating the $\delta^{13}C$ of the fossil fuel component, using:

$$\delta_{ff} = \frac{\delta_{xs} - \delta_{bio}*(1-F_{ff})}{F_{ff}} \quad (7)$$

where F_{ff} is the fraction of C_{xs} due to emissions from fossil fuel combustion, as calculated from the $^{14}CO_2$ data. The values for δ_{xs} are the seasonal $\delta^{13}C$ values from the MT analyses and δ_{bio} is taken to be -26.6 ‰, the average $\delta^{13}C$ of the ambient air plus the discrimination of -16.8 ‰ for the biosphere (Bakwin et al., 1998). This value represents data from temperate northern latitudes (28 – 55 °N), dominated by C3 plants with some C4 grasses present (Bakwin, et al., 1998). Indeed, grasses in southern California are mostly C3 ryes, fescue, and bluegrass, with some C4 grasses such as St. Augustine (www.cropsreview.com/c3-plants.html, last accessed January 25, 2016). The proportions of CO_2 emitted by petroleum and natural gas combustion are calculated using the $\delta^{13}C$ values:

$$\delta_{ff} = F_{pet\,ff} * \delta_{pet} + (1 - F_{pet\,ff}) * \delta_{ng} \quad (8)$$

$$F_{pet\,ff} = \frac{\delta_{ff} - \delta_{ng}}{\delta_{pet} - \delta_{ng}} \quad (9)$$

with an analogous equation for $F_{ng\,ff}$. where $F_{pet\,ff}$ and $F_{ng\,ff}$ are the fractions of petroleum and natural gas combustion contributions in C_{ff}, respectively. The values of δ_{ng} and δ_{pet} used were -40.2±0.5 ‰ for natural gas (Newman et al., 2008; covering measurements in 1972-1973 and 1999) and -25.5±0.5 ‰ for petroleum combustion (average of measurements in (Newman et al., 2008; measurements in 2005), and -26.0, -25.1, and -25.5 ‰ measured in 2007, 2012, and 2014, respectively). The C_{ff}, C_{pet}, and C_{bio} components were corrected for the presence of 10 % ethanol in California gasoline by

multiplying C_{pet} by 0.067 (the fraction of CO_2 emitted by burning the ethanol portion of the ethanol-gasoline mixture; EIA, 2015) to give the amount, in ppm, of CO_2 that was included in C_{bio} but should have been attributed to C_{pet}. The same amount was deducted from C_{bio}. The magnitude of this correction is 0.5 – 1.2 ppm, averaging 0.84 ppm, which represents approximately a quarter of the C_{bio}, but the latter is very small, averaging 3 – 4 ppm and the correction does not affect our results with respect to C_{pet} and C_{ng}.

2.3.4 Time series analysis

We used the algorithm of Jiang et al. (2008) to study details of the average annual patterns of the total CO_2 and C_{ff} in Pasadena, in order to compare with patterns at sites with less contribution from regional fossil fuel combustion, such as Palos Verdes and La Jolla background. This method uses the first three Legendre polynomials and harmonic terms to decompose the signal (Prinn et al., 2000). The harmonic terms define the seasonal and semi-annual cycles, which we compared to results of the same analysis for flask data from La Jolla, CA (Keeling et al., 2005).

To determine trends in the C_{ff} time series, derived from the radiocarbon data, we used the empirical mode decomposition (EMD) method (Huang et al., 1998; Kobayashi-Kirschvink et al., 2012). Using this method, nonlinear and nonstationary time series can be broken down into intrinsic mode functions (IMFs) with increasing period lengths and, finally, to a long-term trend with at most only one minimum or maximum with slope of zero. The algorithm involves using cubic splines to calculate maximum and minimum envelopes for the data series. The average of these envelopes for each time is subtracted from the original or the previous iteration. This process is repeated until the average is a

horizontal line, giving the first IMF. This IMF is subtracted from the raw time series (or previous starting point) and then repeated until the resulting IMF has only one maximum or minimum in the series, the long-term trend. High frequency modes are removed first, with the earliest representing noise. The later modes are interpreted in terms of known processes, such as annual cycles (e.g., IMFs 3 and 4). Following Wu and Huang (2009), we added random noise equivalent to the error in the measurements to create 300 time series, for which the ensemble EMD (EEMD) analyses were averaged. The EEMD technique is data adaptive, not assuming any shape for the IMFs.

3 Results and discussion

The purpose of this project was to determine the sources of C_{ff} in the Los Angeles basin and compare them with bottom-up inventories and data products from government agencies and the scientific community. Below, we compare results of source allocation from the two sites and then examine the temporal variability at the Pasadena site, with its 8-year record. Then we compare the results with government inventories and with the high-resolution Hestia-LA emissions product.

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3.1 Spatial variations – comparison of source attribution at the Pasadena and Palos Verdes sites

The $\Delta^{14}C$ time series for the two sites are shown in Fig. 3c and d, 8 years for Pasadena and 4 years for Palos Verdes. The two data sets are very different, with Palos Verdes radiocarbon results being significantly higher than those in Pasadena except during the winter. However, the summer months in Pasadena are characterized by $\Delta^{14}C$ values far from background, i.e., depleted in ^{14}C due to dilution by CO_2 produced by

burning of fossil fuels containing none of the radioactive isotope. There are occasional negative spikes in $\Delta^{14}C$ during the winter. Total CO_2 excess (C_{xs}; Fig. 4), determined as CO_2 concentration minus background, is similarly disparate with respect to timing. The total enhancement at both Pasadena and Palos Verdes, C_{xs}, spikes during winter (up to 65 ppm and 34 ppm, respectively), but the Pasadena excess also peaks during the summer (up to 43 ppm), whereas Palos Verdes values for C_{xs} are at a minimum during the warm months (3-20 ppm). When the ^{14}C and C_{xs} information are combined to calculate CO_2 emissions due to fossil fuels (C_{ff}; eqn. 3; Fig. 4), we see summer maxima for C_{ff} in Pasadena, but not in Palos Verdes. The spikes in C_{xs} and C_{ff} during fall and winter seasons are not the general trend in Pasadena, as evidenced by the quarterly averages (Fig. 6b). The amount of C_{ff} in the Pasadena seasonal averages (Fig. 4a, 6b) ranges from (18.9 ± 1.2) ppm (winter) to (26.8 ± 0.4) ppm (summer). In Palos Verdes, C_{ff} averages (5 ± 3) ppm during the warmer months and (12 ± 5) ppm during the winter months (Fig. 4b). However, CO_2 emissions from the biosphere (C_{bio}) tend to be higher during the cooler months at both sites (Fig. 4). Refer to Section 3.2 for more discussion of the biosphere's contribution to C_{xs} in Pasadena.

The explanation for the differences in the seasonal cycles of C_{xs} and C_{ff} at the two sites is probably the different wind patterns for the different times of year. Figure 7 shows back trajectories ending at 1400 PST in Pasadena (Fig. A2 for both sites), calculated using NOAA's HYSPLIT model (Draxler and Rolph, 2014; Rolph, 2014), for January and July 2011. These are representative of these months in all years of this study. Wind directions during July are from the west-southwest, whereas they are mostly from the northeast but much more varied during the winter. Thus, in Pasadena, elevated

421 C_{xs} and C_{ff} values during the summer result from air masses traveling across the Los
422 Angeles basin, picking up emissions and transporting them inland. During the winter, the
423 airflow is more mixed, resulting in lower average C_{ff} signals in Pasadena, since a
424 significant proportion of the winds bring less polluted air from the much less populated
425 mountains and deserts located to the north (Santa Ana winds) (Fig. 7). The summer
426 westerly winds bring ocean air to the Palos Verdes site, characterized by CO_2 mole
427 fractions and $\Delta^{14}C$ very similar to background marine air. During the cooler months, the
428 Santa Ana winds from the northeast occasionally blow over the LA basin, bringing its
429 emissions to the coastal site (Fig. 7). This pattern results in more scatter in the magnitude
430 of CO_2 excess observed during the winter at the Palos Verdes site, than during the
431 summer. Figure 8 shows the average annual pattern for C_{ff} at the two sites,
432 demonstrating the effect of the varying wind direction patterns.
433
434 **3.2 Attribution of CO_2 excess from different anthropogenic sources for**
435 **Pasadena**
436 Since we have information regarding the relative contributions of fossil fuel
437 combustion and biosphere respiration from the radiocarbon data, we can use the
438 differences in the $\delta^{13}C$ of the CO_2 to look at the contributions of petroleum/gasoline
439 versus natural gas combustion. We use the MT approach to distinguish between different
440 fossil fuel sources of CO_2 (Miller and Tans, 2003). As described in section 2.3.3, the MT
441 slope of the correlation gives the $\delta^{13}C$ of the local source of CO_2 emissions. In many
442 cases it is difficult to distinguish the anthropogenic sources because the biosphere's
443 signal can overlap that of petroleum. However, in a megacity such as the Los Angeles

444 basin, the contribution of the biosphere to the total CO_2 enhancement can be minimal
445 (≤20 % in Pasadena; Newman et al., 2008; Newman et al., 2013) during the afternoon,
446 when the boundary layer is deepest and most thoroughly mixed. In this study, we use the
447 information from $\Delta^{14}C$ presented above to further constrain the biosphere's input. Since
448 the other major anthropogenic sources (cement production and combustion of coal) are
449 not present in the Los Angeles basin, $\delta^{13}C$ from MT plots can be used to differentiate the
450 proportions of natural gas and oil burned in the region, as discussed below.

451 Seasonal MT slopes for the mid-afternoon Pasadena samples from 2006 through
452 2013 are shown in Fig. 6a. We do not present similar analysis for the Palos Verdes data
453 because it is a shorter data set, with only 3-5 measurements per month (12 per season),
454 and the range in CO_2 mole fractions during the warmer months is less than 20 ppm for all
455 spring and summer seasons. Thus there are insufficient meaningful data to produce a
456 significant trend. Vardag et al. (2015) came to this same conclusion for a rural site in
457 Germany, based on a modeling study.

458 The $\delta^{13}C$ values from MT regressions for the cooler portions of the year in
459 Pasadena are almost always higher than those for the warmer portions. The values for the
460 cooler seasons average (-30.6 ± 0.5) ‰, 1.8 ‰ higher than the average for the warmer
461 months, (-32.4 ± 0.6) ‰. Assuming that there is no contribution from respiration and
462 that the $\delta^{13}C$ of the high-CO_2 end members are -40.2 ‰ for natural gas and -25.5 ‰ for
463 petroleum combustion, as discussed above, then the proportion of natural gas burned in
464 C_{xs} is 32 % during the cooler months and 45 % during the warmer months. The larger
465 fraction of natural gas burned during the warm part of the year is consistent with the
466 observed burning of more natural gas for electricity generation during summer months, as

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Deleted: Newman et al. (2008) showed that no biospheric input was required to explain the $\delta^{13}C$ of mid-afternoon CO_2 during 1972-73 and 2002-2003, although up to 20 % was allowed by the uncertainties.

would be required to power air conditioning needs. Mild winters in this climate require less natural gas combustion for heating buildings, thus minimizing a large winter peak frequently seen in colder regions, such as Salt Lake City, UT (Pataki et al., 2003; Bush et al., 2007) and Chicago, IL (Moore and Jacobson, 2015). This attribution of the different contributions to C_{ff} still does require knowledge of the $\delta^{13}C$ value of the biosphere. As mentioned above, we use a discrimination of 16.8 ‰, the average determined by Bakwin et al. (1998) for northern mid-latitudes and includes a mix of C3 and C4 metabolism plants, dominated by C3. More C4 plants will raise the C_{ng} curve and lower the C_{pet} curve, since the discrimination by C4 plants is much lower (Farquhar et al., 1989).

As mentioned above, we can use the information provided by the $^{14}CO_2$ data to put better constraints on contributions from the biosphere. The calculations based on $\Delta^{14}C$ data in Fig. 6b show that the maximum biosphere contribution was during winter 2012-2013, 7 ppm (28 % of the total C_{ff}), and the minimum was 0.1 ppm during spring of 2010. The average is (4.1 ± 0.5) ppm (16 % of C_{ff}) during cooler months and (2.2 ± 0.3) ppm (8 % of C_{ff}) during warmer months. The seasonality could be due to variations in emissions from the biosphere. However, it is probably due to a more complex combination of emissions and uptake.

The observation that there are seasonal patterns to the CO_2 emissions from combustion of petroleum and natural gas has implications for the effective composition of $\Delta^{14}C$ from fuel combustion. The value for fossil fuels is taken to be -1000 ‰, since they contain no ^{14}C. However, because we have 10 % modern ethanol in our gasoline, and there is seasonal variation in the ratio of gasoline to natural gas usage, there is actually a seasonal variation in radiocarbon from the bulk fuel combustion component.

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And at no time is the $\Delta^{14}C$ value actually that of pure fossil fuel (-1000 ‰). The average value is -954 ‰, and spring-summer periods average 33 ‰ higher than autumn-winter (-939 – -972 ‰, respectively). These seasonal and overall values for $\Delta^{14}C$ of the fuel component were determined as the best-fit values from the individual C_{ff} data to the seasonal mass balance calculations of C_{pet} and C_{ng}.

3.3 Average seasonal and semi-annual patterns

The emissions of CO_2 by anthropogenic processes significantly modifies the annual cycle of CO_2 observed in the Los Angeles region relative to the oceanic air that enters the basin, as exemplified by the background air sampled in La Jolla, CA (Keeling et al., 2005; see discussion in section 2.3.1). There is very little seasonal variability in Pasadena (Fig. 9a). Whereas the average background annual cycle is characterized by a peak in April and drawdown in August-September, with an amplitude of 11 ppm (Fig. 9g), the Pasadena cycle is noisy and relatively flat, with lower CO_2 mole fractions in January-April and high values the rest of the year and only an amplitude of 5 ppm (Fig. 9a). Each pattern can be modeled well using the Legendre polynomial/harmonic analysis of Jiang et al. (2008; Fig. 9b, h). The sum of the seasonal and semi-annual harmonic terms reproduces the data very well, with r^2 values of 0.70 and 0.91 for Pasadena and background, respectively. The average annual cycles are 6 months out of phase, whereas the semi-annual oscillation cycles look very similar at the two sites. The seasonal cycle in Pasadena is consistent with influx of combustion CO_2 during the hot summer months due to increased burning of natural gas at power plants located dominantly in the southwestern portion of the LA basin (CEC, 2015). In contrast, the background data

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reflect global patterns with a drawdown in CO_2 during the summer growing season in the northern hemisphere. Jiang et al. (2012) concluded that the semi-annual oscillation at NOAA's GLOBAL-VIEW sites is due to the combination of gross primary production and respiration of the biosphere. During the winter season, photosynthesis is largely reduced. The peak for gross primary production is relatively flat in winter. However, CO_2 is still emitted to the atmosphere by respiration from the biosphere in winter, which has a relatively sharp peak compared with the photosynthesis term. Thus the combination of gross primary production and respiration leads to the double peaks in each year in the net ecosystem production, which contributes to the semi-annual oscillation in CO_2 (Jiang et al., 2012). The semi-annual oscillation in the background signal is consistent with this interpretation. We see virtually the same pattern in Pasadena, although the amplitude is smaller, consistent with the small biospheric contribution indicated by the $\Delta^{14}C$ results.

Based on the work of Jiang et al. (2012) we expect the annual cycle in Pasadena to be larger in amplitude than in La Jolla since it is further north, but the amplitude is actually much smaller. If the regional emissions of CO_2 in Pasadena are relative to a La Jolla background, then there is a huge enhancement during the summer! Indeed, the seasonal cycle for C_{ff} (Fig. 8) is 11 ppm, with the peak in August-September, and there is very little semi-annual oscillation.

The annual pattern for CO_2 in Palos Verdes is also heavily influenced by the transport of combustion emissions from the Los Angeles basin (Fig. 7, 8, 9c, d). The average monthly pattern is more similar to the background's (Fig. 9g, h) than to Pasadena's (Fig. 9a, b). However, there is a strong peak in the winter that is consistent

with the increased number of days during this time of year with winds from the north to east, travelling over the basin. Doing the same analysis for the monthly minimum values (Fig. 9e, f) gives a pattern that is much more similar to the background's, confirmed by the comparison of the raw data with the background smoothed time series in Fig. 3. This supports use of minimum values from Palos Verdes as reasonable background for the Los Angeles basin. The C_{ff} annual pattern is inverse to that in Pasadena, as expected by the seasonal wind patterns (Figs. 7, 8).

The conclusion of this analysis of the annual cycles is that the Pasadena CO_2 pattern is significantly different from the natural cycles observed in La Jolla background and show very little seasonal variation compared with this background. The semi-annual pattern, although smaller in amplitude than expected, is in phase with that observed in the background, which we suggest might reflect a reduced biosphere signature in Pasadena due to artificial irrigation, which may reduce seasonality expected due to wet and dry parts of the year. Both the Pasadena and Palos Verdes average CO_2 patterns reflect the seasonal changes in wind patterns, whereas the monthly minimum Palos Verdes pattern is that expected for the background air entering the LA basin. It will be interesting to see whether water restrictions put into effect during summer of 2015 because of an on-going, severe drought (ca.gov/drought, 2015), affect the patterns observed in the future.

3.4 Temporal trends in CO_2 excess observed in Pasadena

3.4.1 Long-term time series analysis

In order to discern the long-term trends in fossil-fuel CO_2 excess, we must first remove noise and the periodic signals discussed above from the record. We used

empirical mode decomposition (EEMD; Huang et al., 1998; Kobayashi-Kirschvink et al., 2012), as described in the calculation section above, on the 8-year time series of C_{ff} (Fig. 4a) to identify intrinsic mode functions (IMFs; summary in Fig. 10a-d; full results in Fig. A3). The noise is represented by the first and second modes (IMF 1 and IMF 2). Combination of the third and fourth modes of the C_{ff} time series (IMF 3 and IMF 4) correlates significantly with the 30-day average record for temperature measured at the top of the 9-story library next to the sampling site ($r^2 = 0.6$). Note that there are severe mode mixing problems in IMF3 (e.g. during 2011–2013) between the dominant annual cycle and subseasonal variations, which also affects the nonlinear decompositions in the higher modes. To minimize the effects of mode mixing on the extractions of inter-annual trends, we perform the EEMD again after removing the average annual cycle (minus the mean of the raw data), defined as monthly averages over the entire time period (2006-2013; resulting time series shown in Fig. 10e). The revised inter-annual trend is shown in Fig. 10f. The sum of the trend + IMF 6 is a curve with increasing C_{ff} values leading up to mid-2007, when they began to fall, until leveling off in 2010 and perhaps starting to rise towards the end of the time series. There are end effects in this method, such that we do not have confidence in the first and last years of the analysis. The uncertainties in this calculation are shown by the shaded regions in Fig. 10f. These were determined as the 1σ standard deviations of adding random noise equivalent to 13.7 % to the data 300 times and then running the EMD analysis. The 13.7 % noise added is the uncertainty of the C_{ff} values calculated from $\Delta^{14}C$, ± 1 ppm, relative to the standard deviation of the data, 7.3 ppm. The maximum and minimum values are distinct at approximately the 2σ standard deviation level, as shown in Fig. 10f and indicate a significant decrease of 9.5 % between

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593 the maximum in May 2007 and the average for January-June 2010. Using different
594 backgrounds for $\Delta^{14}C$, such as extrapolating the data from La Jolla (Fig. 5) does not
595 significantly affect this analysis, resulting in differences of (0.01 ± 0.09) ppm C_{ff} out of a
596 range on the order of 2 ppm. And our result showing that there are different values of
597 $\Delta^{14}C$ for bulk fuel for autumn-winter than for spring-summer also does not change these
598 conclusions, since the RMSE of the IMF6+trend (Fig. 10f) using different $\Delta^{14}C$ for cool
599 vs. summer months relative to the constant average value is 0.1 ppm C_{ff}.
600 The timing of the drop in the fossil-fuel CO_2 excess around 2008 is consistent
601 with the economic recession in late 2007-2009 (NBER, 2010) with slow recovery
602 beginning in 2010. Similar results for global CO_2 emissions due to fossil fuel combustion
603 have been documented by Peters et al. (2012) and Asefi-Najafabady et al. (2014). The
604 fraction of decrease in C_{ff} (9.5 %) is similar to, although less than, the decrease in global
605 GDP during this time (global GDP decreased by 13 %; World Bank, 2015).
606
607 **3.4.2 Comparison with inventories and bottom-up gridded C_{ff} data**
608 A major goal of this study is to compare trends in top-down measurements such
609 as those described here with bottom-up estimates in order to understand how to bring
610 them together in space and time for direct validation. Annual averages of the seasonal
611 amounts derived for C_{ff}, C_{pet}, and C_{ng} compare well in relative proportions to the averages
612 from California's state inventory provided by the California Air Resources Board
613 (CARB, 2015). Annual values for CO_2 emissions from all fossil fuels, on-road
614 transportation, and natural gas consumption for the entire state of California, through
615 2013, are superimposed on the seasonal averages for C_{ff}, C_{pet}, and C_{ng} in Fig. 11. The

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Deleted: The observation that C_{ff} does not decrease by as large a percentage as the economy is consistent with the analysis of York (2012) that anthropogenic emissions are asymmetric with respect to economic growth and decline. Increases in emissions that come during growth periods are not matched by declines of the same magnitude during economic downturns, because high consumption durable goods that are put in operation during growth remain in use during the decline.

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decrease in total fossil fuels combustion between 2007 and 2011 in the State's inventory is 11 %, very similar to the 9.5 % decrease indicated by the EEMD time series analysis of our C_{ff} results above. There is a difference in timing between the data presented here (2010) and those from the CARB inventory (2011-2012) that may be due to uncertainties in the data or to the different domains covered by the two data sets. The relative proportions of the on-road portion of the CARB budget is 57 % of fossil fuel CO_2 emissions and the petroleum portion of our top-down estimate averages 54 % of C_{ff}. This inventory is for the entire state, not the LA basin, and it includes annual values only. This discussion has focused on inter-annual variations in C_{ff}, although, as we have shown in Fig. 7 and 8, there are at least seasonal variations in wind direction. Looking at back trajectories from the entire time period of this study, we see no significant shifts in the winds, from year to year although systematic modeling has not yet been done and is beyond the scope of this paper. Next, we look at finer spatial and temporal scales.

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Seasonal variations in C_{pet} concentration at the Pasadena location can be compared to the variation in emissions compiled by various sources. Figure 12 presents a comparison of the C_{pet} concentration to the petroleum and on-road CO_2 emissions components estimated by the Energy Information Administration (EIA) (EIA, 2015), the State of California (CARB, 2015), and the Hestia-LA project (K. R. Gurney, personal communication). Comparison of the seasonal averages for petroleum consumption data, based on deliveries (EIA), and gasoline taxes collected (CBE, 2014) with C_{pet} indicates similar decreases of 10-20 %, but with a lag of a few months (Fig. 12). The lag could be due to the different domains of the data sets: EIA and State of California data reflect the

entire state domain while the Hestia C_{ff} data product reflects the LA Basin specifically, and the atmospheric data presented here represents air sampled in Pasadena.

To truly understand the observations in Pasadena, we must combine information from spatial and temporal meteorological and C_{ff} databases, such as obtained using a model like the Weather Research and Forecasting (WRF) model. Since this is beyond the scope of this work, we have used the information from HYSPLIT back trajectories (Fig. 7; January and July) to provide rough limits for winds arriving in Pasadena at our sampling time of 14:00 PST. These back trajectories suggest that prevailing winds during the summer come from the southwest, across the basin, and winds during the winter come from the northeast, across the mountains from the desert. We have looked at 1.3-km x 1.3-km gridded C_{ff} from the Hestia-LA data product to qualitatively determine what relative emissions from petroleum combustion are expected during January and July for the two years of the Hestia data (2011 and 2012). These are plotted in Fig. 12 and agree in seasonality with the observations presented here: more C_{pet} is observed during the summer than during the winter. A map of the regions selected for January (NE) and July (SW) is presented in Fig. 13a, along with the HYSPLIT back trajectories for January and July, 2011, and the monthly average CO_2 emissions due to total petroleum combustion (the Hestia-LA product) from the two integrated areas based on the wind directions are shown in Fig. 13b for years 2011 and 2012.

We show comparison of the C_{ng} results from Pasadena with area-integrated bottom-up inventories and the Hestia-LA data product in Fig. 14. The California Energy Commission (CEC, 2015) compiles data for natural gas consumed by power plants throughout the state, including Los Angeles and Orange counties. These seasonal data

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691 are consistent with the detailed Hestia-LA data for the electricity production for the entire
692 Los Angeles basin (dashed dark blue line in Fig. 14a). And the seasonality of all of the
693 inventories involving just the electrical power sector agrees well with the seasonality of
694 the time series for C_{ng} (Fig. 14a), with peaks during the summer and troughs during the
695 winter. The source attribution analysis using $\Delta^{14}C$ and $\delta^{13}C$ also captures the increase in
696 C_{ng} consumption of the power plants in recent years, although the data from this study
697 suggest that the increase started earlier than do the inventories. However, the
698 observations of CO_2 concentration and $\delta^{13}C$ integrate over all natural gas combustion and
699 cannot pick out just this one sector.

700 Overall statewide and Los Angeles basin inventories show maximum natural gas
701 usage during the winter (dashed green line in Fig. 14b). Other sources of combusted
702 natural gas include residential, commercial, industrial, and transportation use, which
703 could affect the trends, but we do not have seasonal data for these in the Los Angeles
704 megacity for the full period of this study. However, the seasonal signal for total
705 emissions from natural gas combustion from the Hestia-LA project for 2011-2012 is
706 consistent with the data presented here, when the seasonal prevailing wind directions are
707 considered. The seasonal pattern of emissions from natural gas combustion at any one
708 location is characterized by a small peak during the cooler months and a trough during
709 the warmer months (Fig. 13c). However, C_{ff} in the region sampled by winds arriving in
710 Pasadena during the winter (the northeast) are always lower than those in the basin, over
711 which the summer winds travel to the sampling site. Therefore, transport of air masses
712 following the seasonal wind patterns can explain the observations in Pasadena. The
713 earlier onset of the increase in C_{ff} from natural gas combustion indicated by the data

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(2010) relative to that indicated by the government inventories might be due to the mismatch in geographical regions, variations in inter-annual atmospheric transport, or deficiencies in the inventories.

Since the seasonal cycle observed in C_{pet} and C_{ng} in Pasadena is probably due to atmospheric transport, modeling of this effect is critical to being able to combine top-down observations and bottom-up economic and usage data for a direct consistency comparison. These effects must be removed in order to understand long-term trends due to variations in anthropogenic emissions. The time series analysis using Empirical Mode Decomposition presented in section 3.4.1 removes the seasonal signals to concentrate on the longer-term signals, which show reasonable agreement with the longer-term trends in the statewide inventory.

4 Conclusion

Detection of anthropogenic excess of CO_2 at two sites in the Los Angeles basin, one on the coast and one inland against a barrier mountain range, reveals significant spatial and seasonal variability due to the biosphere, natural gas combustion, and petroleum combustion. Seasonal patterns in wind direction determine the source region of the excess detected at the two sites. Winds from the west to southwest during the warmer months bring marine air with little excess to Palos Verdes, and these same winds continue across the LA basin picking up emissions from fossil fuel combustion to be observed in Pasadena. During the cooler months, wind directions are more varied and include periods when air with low emissions comes to Pasadena from the northeast to

737 northwest and then travels across the basin to Palos Verdes, incorporating anthropogenic
738 emissions along the way.
739 The nature of the excess changes with season, as reflected by the $\delta^{13}C$ values of
740 CO_2 observed in Pasadena. During warmer months, lower values for $\delta^{13}C$ of the local
741 excess indicate a higher proportion of natural gas burned, consistent with government
742 inventories that indicate more natural gas burned during summer to produce electricity to
743 power air conditioning. Even more importantly, however, the seasonal trends in the
744 fossil fuel combustion observed in Pasadena are consistent with the shift from
745 southwesterly winds during warmer months to northeasterly winds during cooler months.
746 Therefore the source region of emissions changes from the Los Angeles basin during
747 summer to the mountains and desert during winter, for our Pasadena sampling site.
748 Trend analysis by ensemble empirical mode decomposition supports the relationship
749 between emissions and temperature.
750 The long-term trend in CO_2 excess from fossil fuel combustion is consistent with
751 C_{ff} changes associated with the economic recession and slow recovery of 2008 through
752 the present, and indicates a significant decrease of 9.5 % since the maximum in late 2007,
753 consistent with the bottom-up inventory of the California Air Resources Board. Indeed,
754 top-down and bottom-up methods of determining the anthropogenic sources of CO_2
755 emissions must be compared to each other to better understand inconsistencies, potential
756 biases, and uncertainty. Previously, however, comparisons have been limited by the
757 scope of emissions, large and overlapping uncertainty, and differences in the target
758 domain. Here we have shown that combining data from radiocarbon and $\delta^{13}C$ values
759 moves us towards a direct comparison in a megacity with very large emissions.

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Measurement trends at a receptor site are consistent with annual variations in California statewide bottom-up inventories for C_{ff} attributed to petroleum and natural combustion, individually as well as for total CO_2 emissions. Even greater consistency between top-down measurements and granular emission estimates specific for the LA megacity domain are achieved when considering wind direction and sub-city source regions. This strengthens the need to have measurement, modeling, and inventories that are specifically aimed at the same domain with fine space/time resolution.

The next steps are to include modeling with inversion of the measurements to understand the combination of atmospheric transport and emissions and to extend the analysis to a denser network of surface monitoring stations such as the Los Angeles Megacities Carbon Monitoring Project (Kort et al., 2013) and the California Laboratory for Atmospheric Remote Sensing (CLARS) observations from Mount Wilson (Wong et al., 2015). Although the uncertainties are large enough that the method described here will not be usable in non-urban regions, similar to the conclusion of the modeling study by Vardag et al. (2015), anthropogenic C_{ff} dominate significantly over natural processes in megacities. Therefore, this kind of monitoring in megacities will allow society to understand and monitor the sources of the CO_2 that are the major contributors to global warming.

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Acknowledgments

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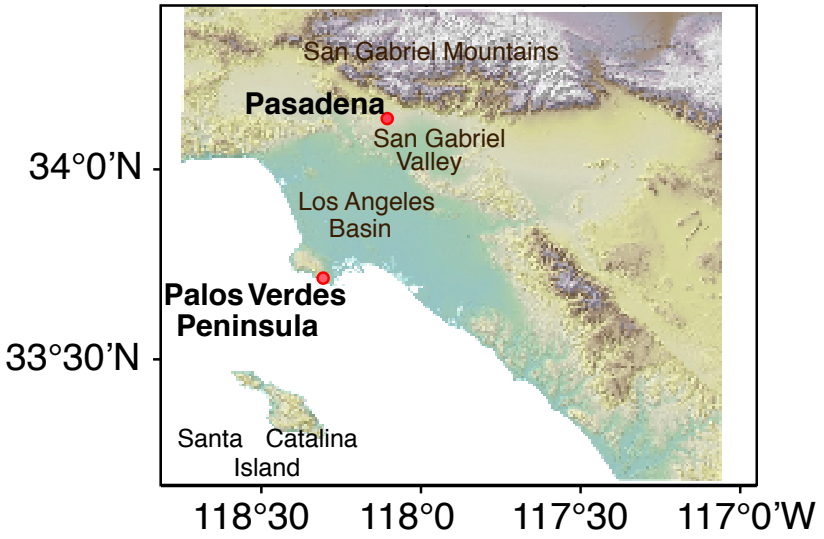
1002 **FIGURES**



1003 Figure 1. Map of southern California, showing sampling locations in Pasadena and Palos
1004 Verdes (red dots).

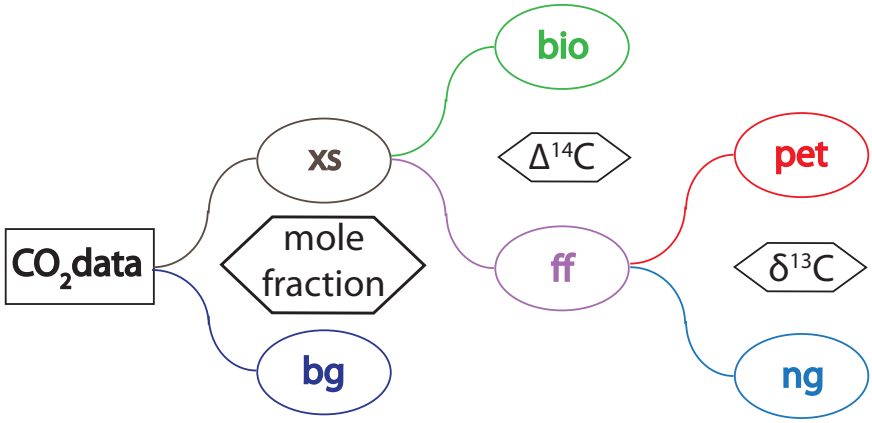


Figure 2. Schematic diagram showing the use of different data sets for attribution of the sources of CO_2 emissions. Mole fractions of background (bg) and observations are used to determine C_{xs} (excess over background/bg); $\Delta^{14}C$ values are used to distinguish C_{ff} (fossil fuel, ff) and C_{bio} (biosphere, bio); $\delta^{13}C$ compositions are used to distinguish C_{pet} (petroleum/gasoline, pet) from C_{ng} (natural gas, ng).

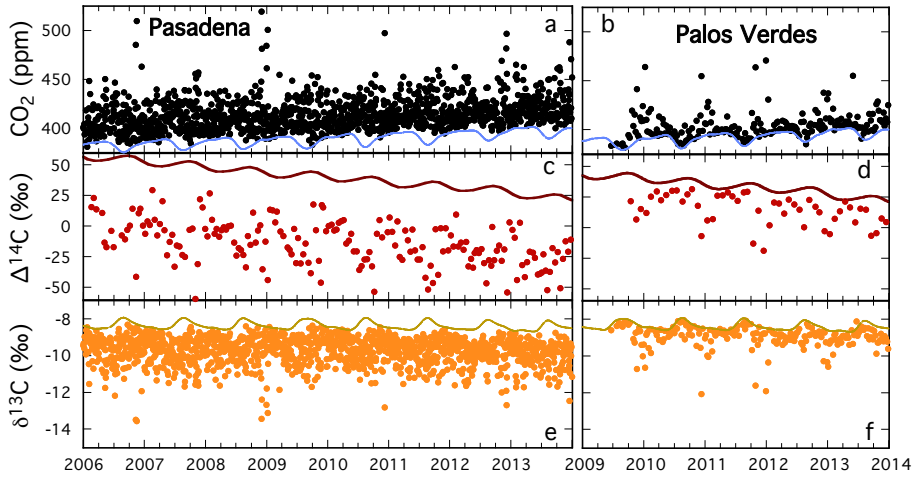


Figure 3. Time series of CO_2 mole fractions for $^{14}CO_2$ samples (a, b), $\Delta^{14}C$ data (c, d), and $\delta^{13}C$ (e, f) for Pasadena and Palos Verdes. The solid curves are backgrounds used in the calculations: $\delta^{13}C$ and CO_2 backgrounds are from La Jolla, CA and $\Delta^{14}C$ from Pt. Barrow, AK.

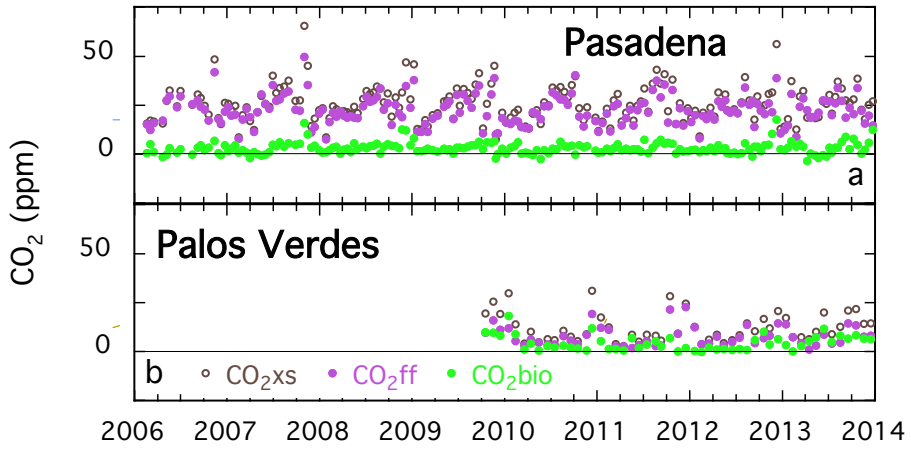


Figure 4. Time series of C_{xs}, C_{ff}, and C_{bio} calculated from $\Delta^{14}C$ (see text for description of calculations) for Pasadena (a) and Palos Verdes (b). The errors for C_{ff} are 1 ppm. The negative C_{bio} values indicate photosynthetic uptake. The value of $\Delta^{14}C$ for fuel for this calculation was taken to be -954 ‰, the average from the summer and winter calculations.

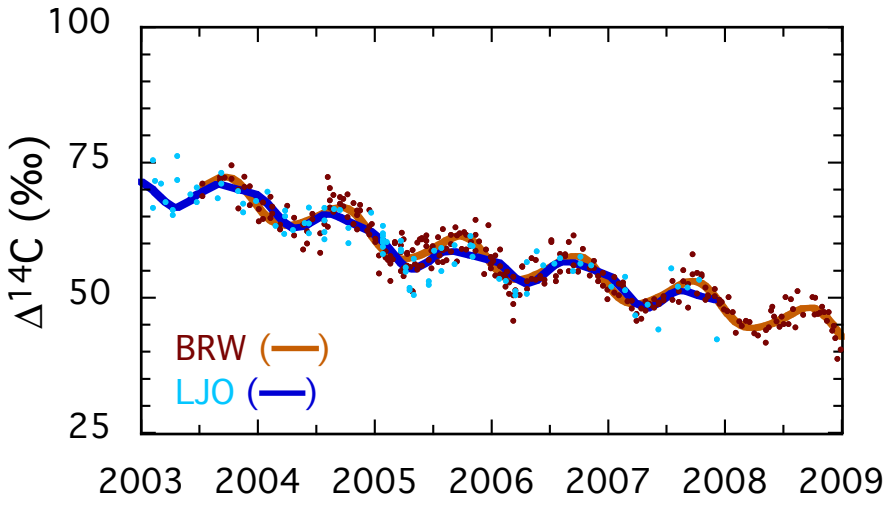


Figure 5. Comparison of possible background records for this study, Pt. Barrow, AK, (BRW; Xiaomei Xu, unpublished data) and La Jolla, CA (LJO; Graven et al., 2012). The smoothed brown curve for BRW is the $\Delta^{14}C$ background used for this study and was calculated using the algorithm of Thoning et al. (1989), from the function plus the smoothed residuals of the long-term trend, using 2 harmonic and 3 polynomial terms in the function and 667 days as the long-term cutoff for the low-pass filter.

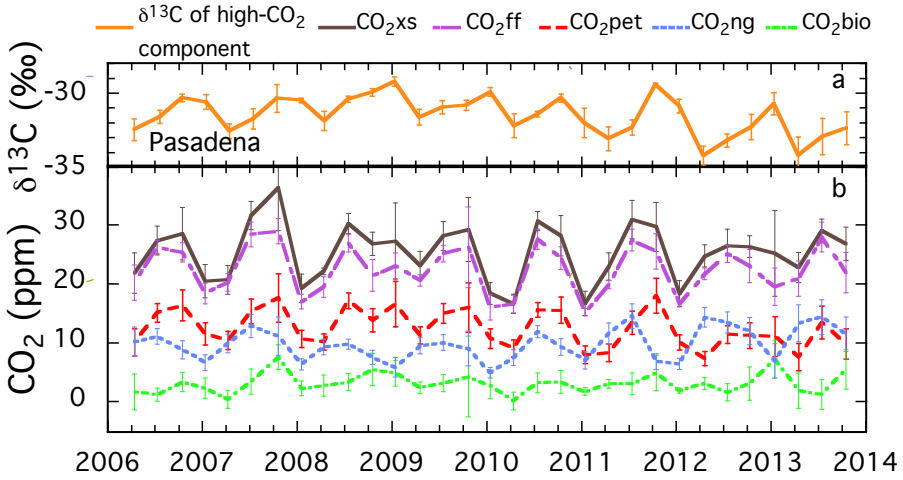


Figure 6. Attribution of CO_2 excess in Pasadena among combustion of natural gas and petroleum and the biosphere. (a) Miller-Tans slopes for seasonal averages of monthly plots. Error bars are standard errors of the regression intercepts. (b) Attribution of C_{xs} among all three sources (natural gas, petroleum, and the biosphere), combining the information from $\Delta^{14}C$ and $\delta^{13}C$, using Miller-Tans slopes to determine the relative proportions of petroleum and natural gas combustion. Error bars are propagated from the errors in the $\delta^{13}C$ intercepts and the $\Delta^{14}C$ measurements.

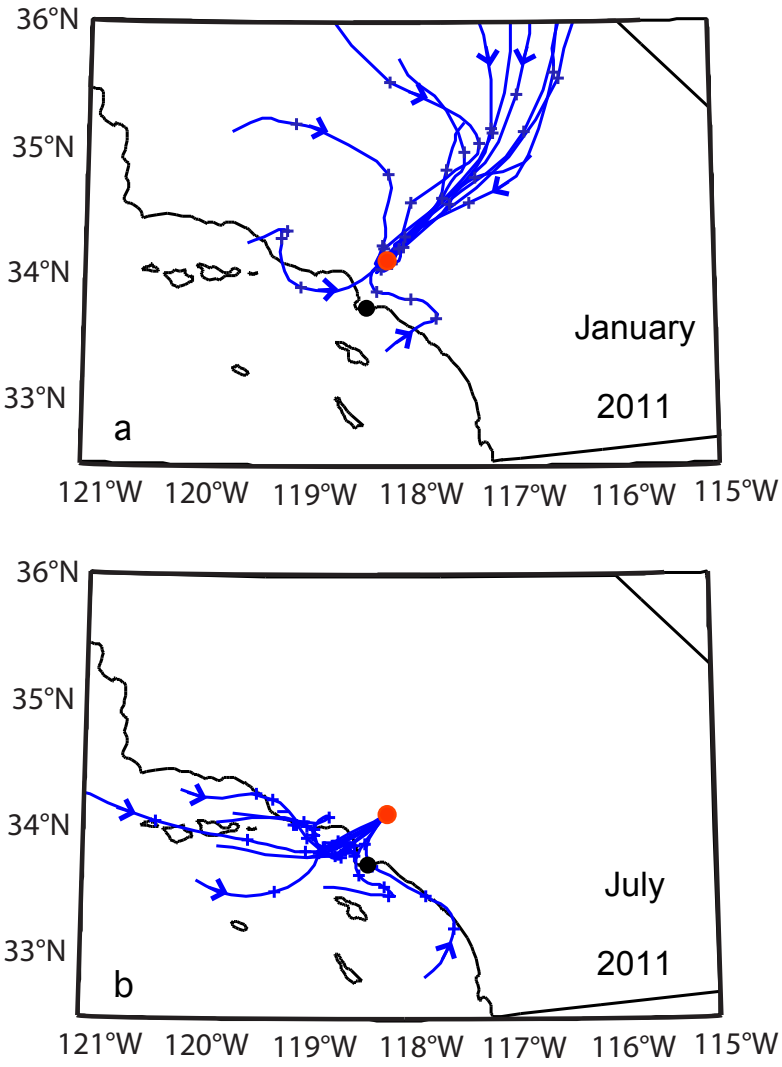


Figure 7. Back trajectories (24 hour) for winds arriving at the Pasadena site (red dot) at 1400 PST for January (a) and July (b) 2011, calculated by HYSPLIT (Draxler and Rolph, 2015; Rolph, 2015) for all sampling days in January and selected sampling days in July, for clarity. Results for all sampling days are shown in Fig. A2. Arrows indicate the direction of air flow. Plus signs indicate 6, 12, and 18 hours from the Pasadena site. The black dot is the location of the Palos Verdes site. The back trajectories for the Palos Verdes site show a similar pattern (Appendix Fig. A2). The back trajectories explain the difference between the annual cycles at the two sites, shown in Fig. 8.

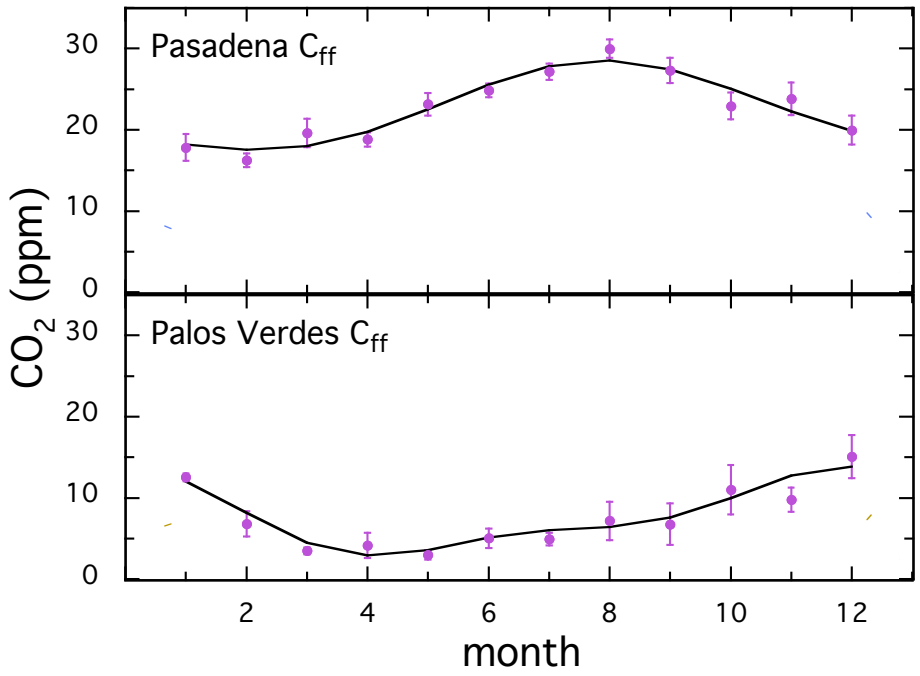


Figure 8. The annual patterns for C_{ff} in Pasadena and Palos Verdes calculated as the best fit of two harmonics plus the average of the annual cycles (black curves). These patterns are consistent with seasonal differences in the back trajectories shown in Fig. 7.

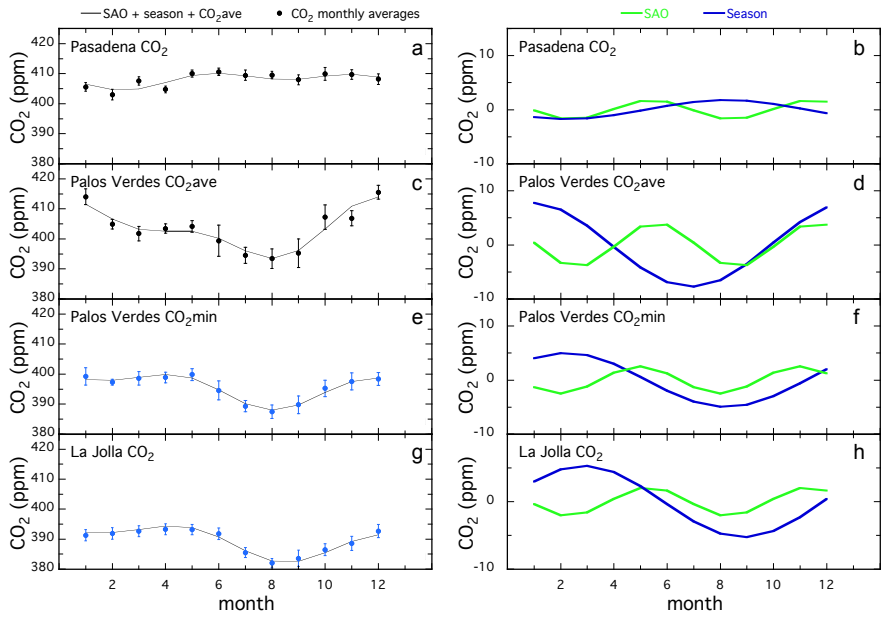


Figure 9. Comparison of seasonal and semi-annual oscillation cycles of CO_2 mole fractions for flask samples from Pasadena (2006-2013) with those at the La Jolla (2006-2013) and Palos Verdes (2009-2013) sites. Left column panels show the average annual patterns for the monthly averages together with the sum of the harmonics for seasonal (blue) and semi-annual (green) cycles (Jiang et al., 2008). Right column panels show the amplitudes and phases of the pure harmonic components. Two sets of results are shown for Palos Verdes, for the monthly averages (c, d) and for the monthly averages of weekly minima (e, f). The monthly averages show the effect of transport on the signal, with a large peak during the winter, while the minima (in blue) show that data from this site are very similar to La Jolla (in blue) and should be a good estimation of the background air for the LA basin. Error bars on the monthly averages of the data are 1σ standard errors.

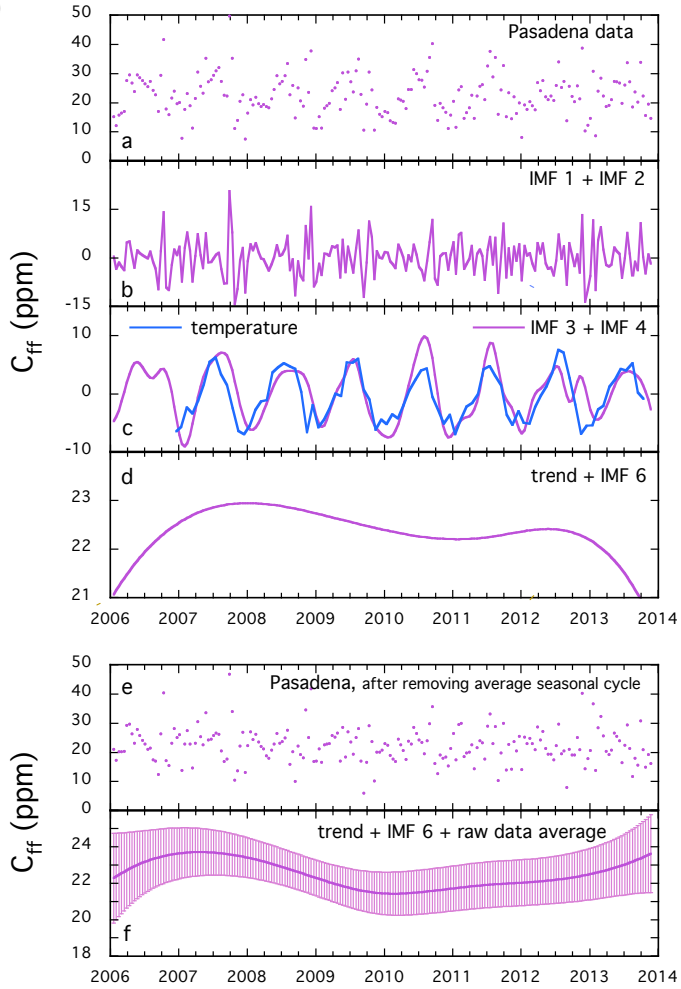


Figure 10. Results of ensemble empirical mode decomposition (EEMD) (Huang et al., 1998; Wu and Huang, 2009) of the C_{ff} time series calculated using Eq. (3) and the average, constant $\Delta^{14}C$ of -954 ‰ for fossil fuel. The top set of panels show the raw data (a), noise (b), annual and semi-annual mode (c), and the trend + IMF 6 (d). The pattern of the trend + IMF 6 shown in (d) is within 1σ uncertainty of no variation over this time period. The bottom two panels include the raw data after subtracting the average annual cycle (centered at zero) (e) and the trend + IMF 6 for the modified data set (f). 30-day average temperatures (minus the overall average and scaled to match the magnitude of the C_{ff} IMF; blue curve) are superimposed on the plot of IMF 3 + IMF 4 (c). Shaded regions in (f) indicate 1σ standard deviation of 300 Monte Carlo realizations with 13.7 % noise added, the ratio of the uncertainty in C_{ff} to the standard deviation of the data.

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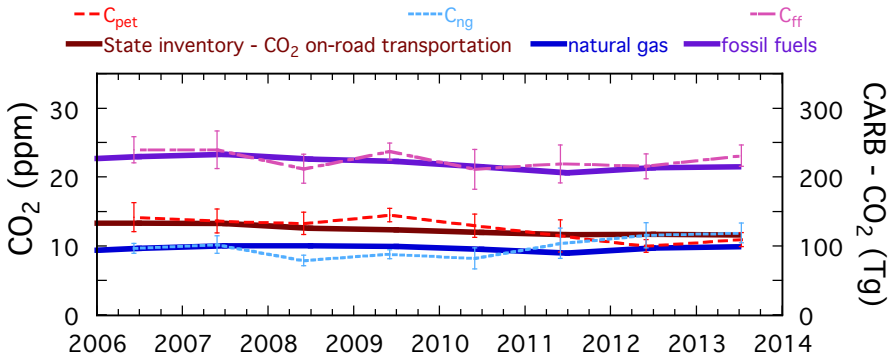

Figure 11. Comparison of annual average CO_2 emissions from bottom-up California Air Resources Board (CARB) inventories (thick lines; right axis labels) for fossil fuel-derived emissions with top-down annual averages from the Pasadena data, using the Miller and Tans (2003) approach to attribute CO_2 emissions from petroleum and natural gas combustion from the $\delta^{13}C$ measurements. Annual curves showing the attribution of C_{xs} averaged from the seasonal values from Fig. 6b are shown as thinner lines. The error bars on the results from the flask sample data are 1σ standard errors of the means. The annual trends from the bottom-up CARB inventories are plotted on a scale exactly 100 times that of the trends derived from the CO_2 measurements, showing that the relative proportions are very similar through 2013.

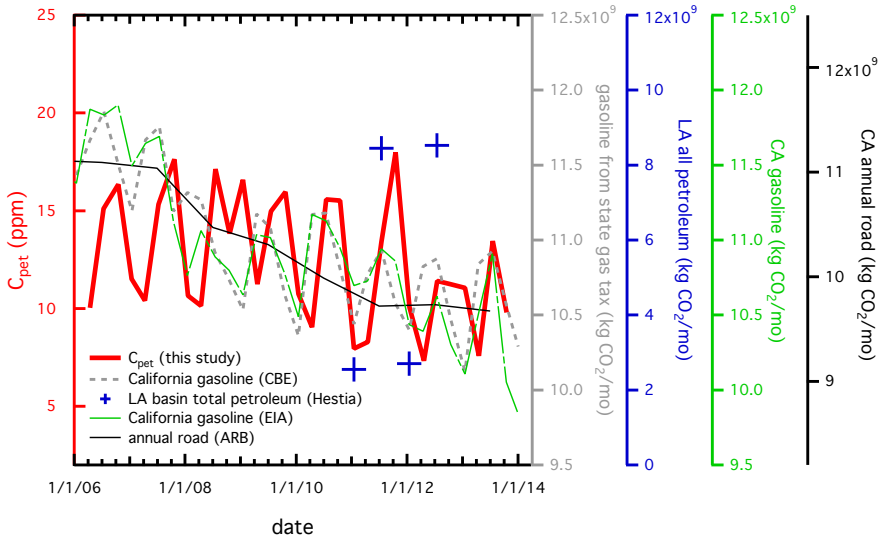

Figure 12. Comparison of the Pasadena C_{pet} atmospheric concentration with all available area-integrated bottom-up fossil fuel CO_2 emissions per month (mo), including gasoline sales based on taxes paid to the California Board of Equalization (CBE, 2014), gasoline provided in California by prime suppliers, the California Air Resources Board's annual road emissions (CARB, 2015), and the Hestia-LA gridded total petroleum. The Hestia-LA data product is specific to the Los Angeles megacity domain; all inventories are statewide estimates. Since the Hestia-LA product is gridded, we show the emissions emanating from different regions for January (northeast quadrant, Fig. 13a) and July (southwest quadrant), based on prevailing winds during those periods (Figs. 7 and 13a). The axis for each inventory has been adjusted to allow easy comparison. The seasonality of the C_{pet} data lags the bottom-up inventories by a few months. This analysis is consistent with the observed decrease in gasoline combustion during 2008-2011.

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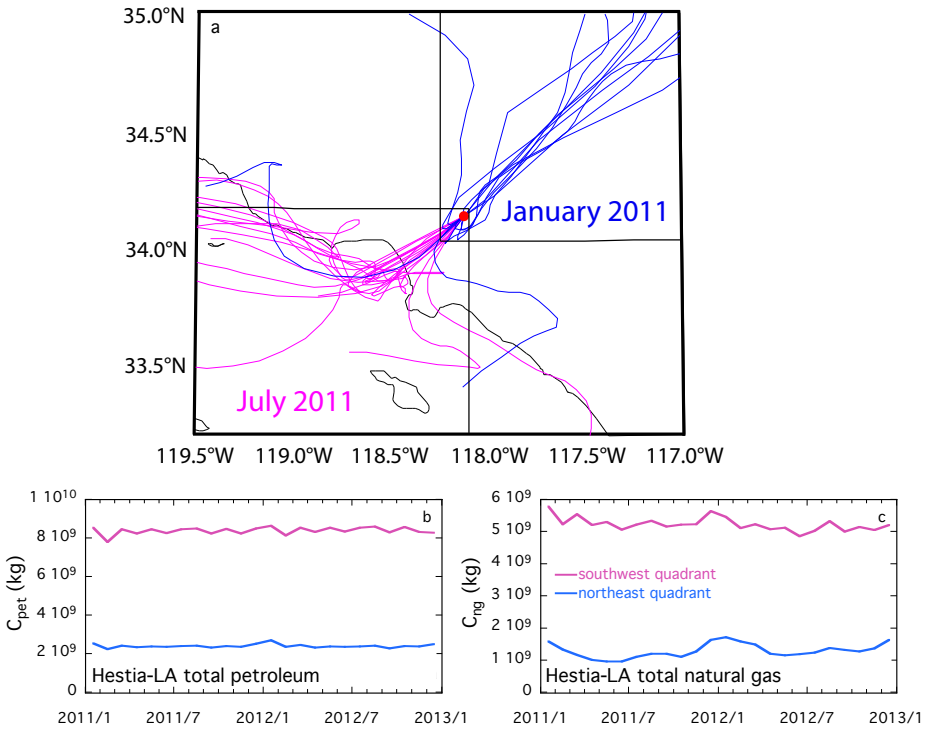

Figure 13. Relevant emissions selection from the Hestia-LA data product. (a) Quadrants selected for investigation of CO_2 emissions from the Hestia-LA data product, together with the 24-hour back trajectories calculated by HYSPLIT for January (northeast quadrant) and July (southwest quadrant) $\Delta^{14}C$ sampling days. The back trajectories end in Pasadena (red dot) at 1400 PST. Monthly averaged time series for Hestia-LA data product C_{ff} are shown from total petroleum combustion (b) and total natural gas combustion (c) for 2011 and 2012. For both the northeast quadrant of the Los Angeles region, the source of winter emissions, and the southwest quadrant, the source of summer emissions, the seasonal pattern is either flat (petroleum) or characterized by peaks during the winter (natural gas). But the summer emissions are always higher than those during winter, consistent with the observed top-down patterns for C_{pet} and C_{ng} in Pasadena.

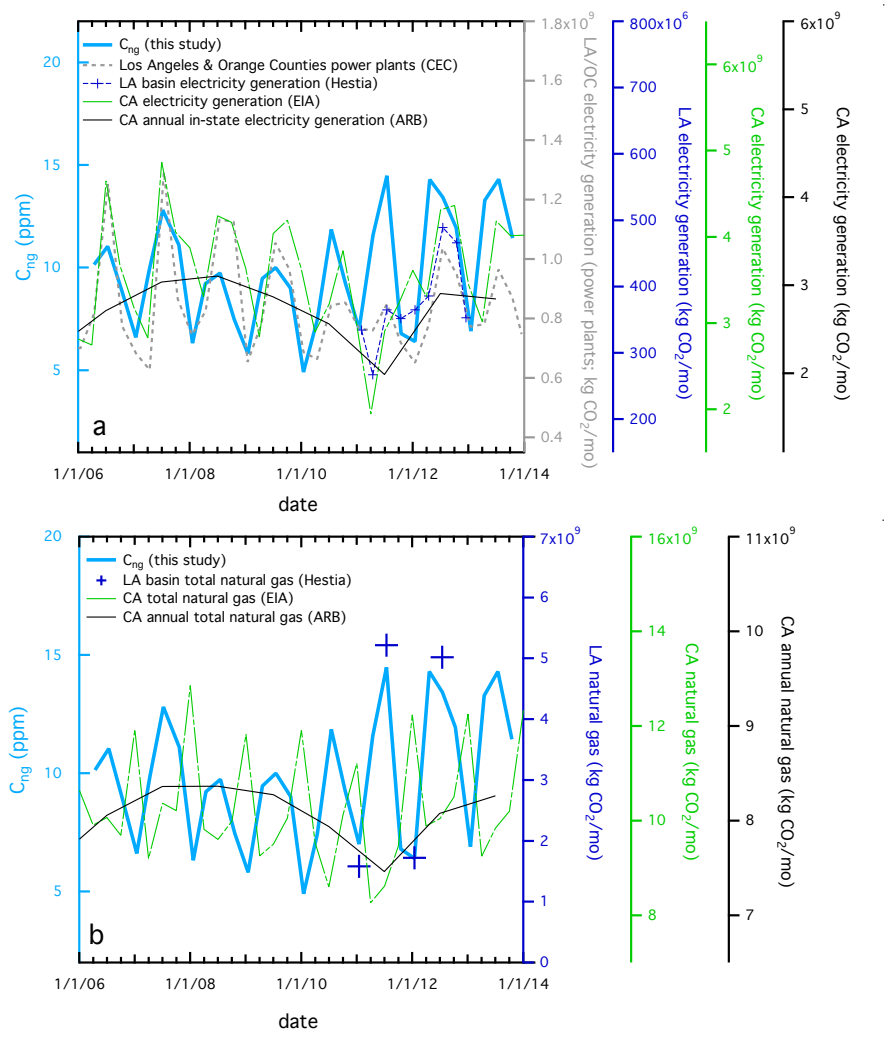

Figure 14. Comparison of Pasadena C_{ng} atmospheric concentration with area-integrated inventories of natural gas combustion, as well as the gridded Hestia-LA data product for southwest and northeast regional sectors for July and January months, respectively, in emissions/month (mo). Panel (a) compares the data from this paper with usage of natural gas by the electrical power sector; panel (b) shows the comparison with total natural gas consumption. Statewide inventories are given by EIA (2014) and CARB (2015) curves. Regional inventories include Hestia results and natural gas from power plants (CEC, 2014) in Los Angeles and Orange counties with monthly data (except Calabasas and Valencia). The vertical axes have been adjusted to allow easy comparison. This analysis is consistent with the increase in natural gas usage during the last few years.

Appendix

1. Monthly Miller Tans plots for 2011

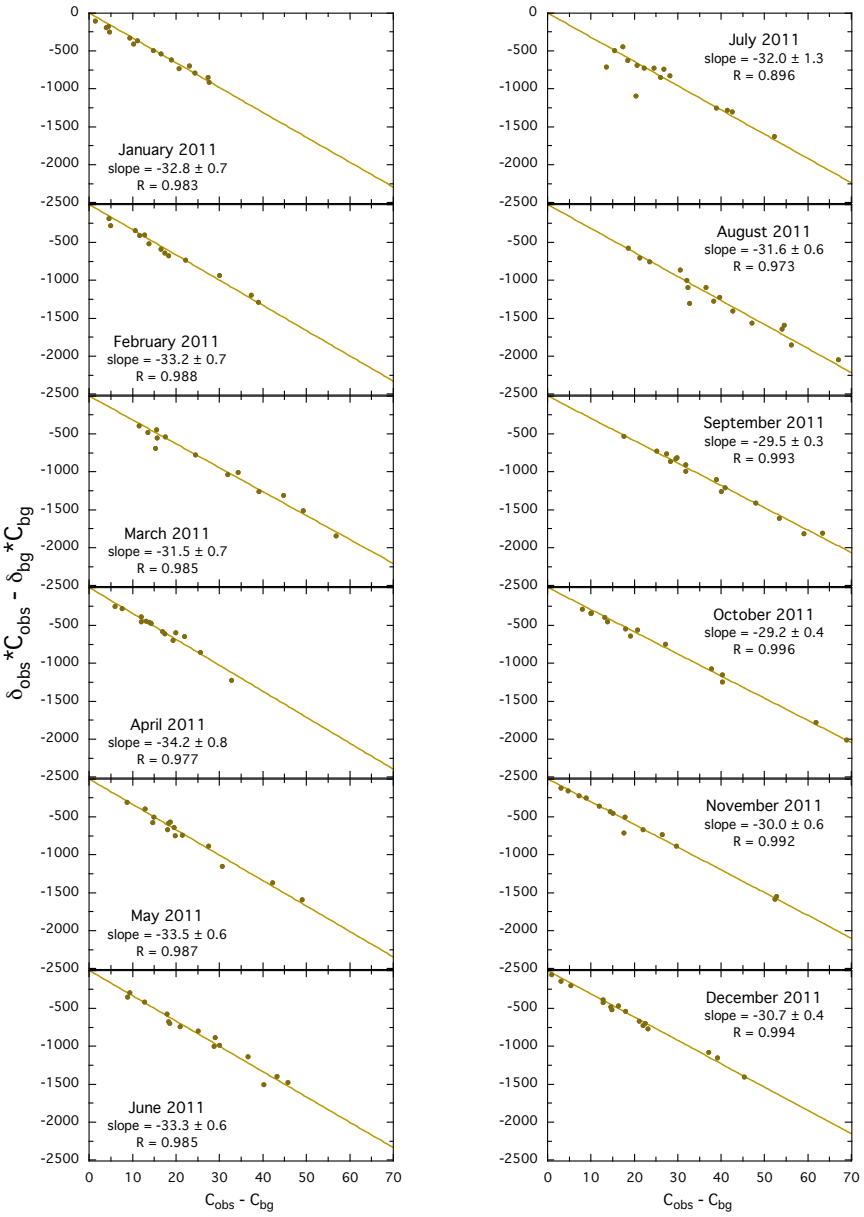

Figure A1. Miller-Tans plots for each month in 2011. Values of the slopes for three-month seasonal averages are plotted in Fig. 6a.

2. Back trajectories for both Pasadena and Palos Verdes sites

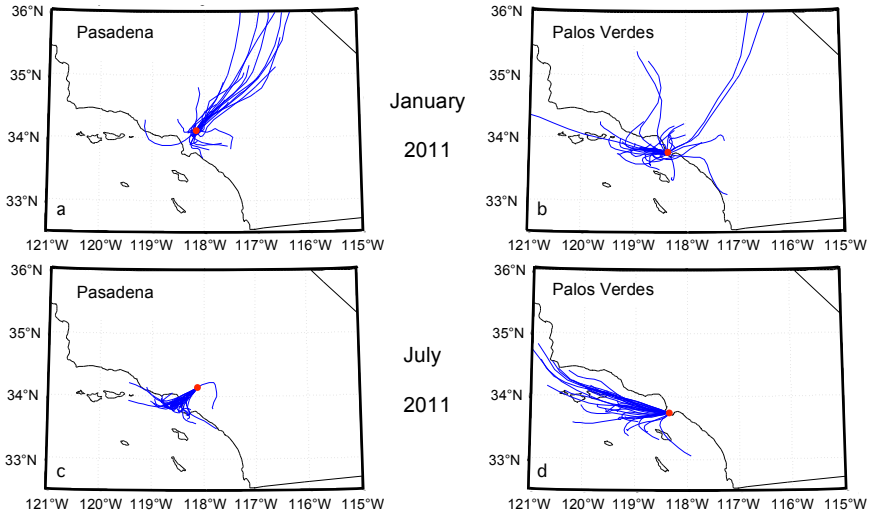

Figure A2. Twelve-hour back trajectories for all days in January and July, 2011, for the Pasadena and Palos Verdes sites. This shows more detail for the effect of transport on the air masses sampled during summer and winter at the Palos Verdes site than Fig. 7.

3. Full ensemble empirical mode decomposition results

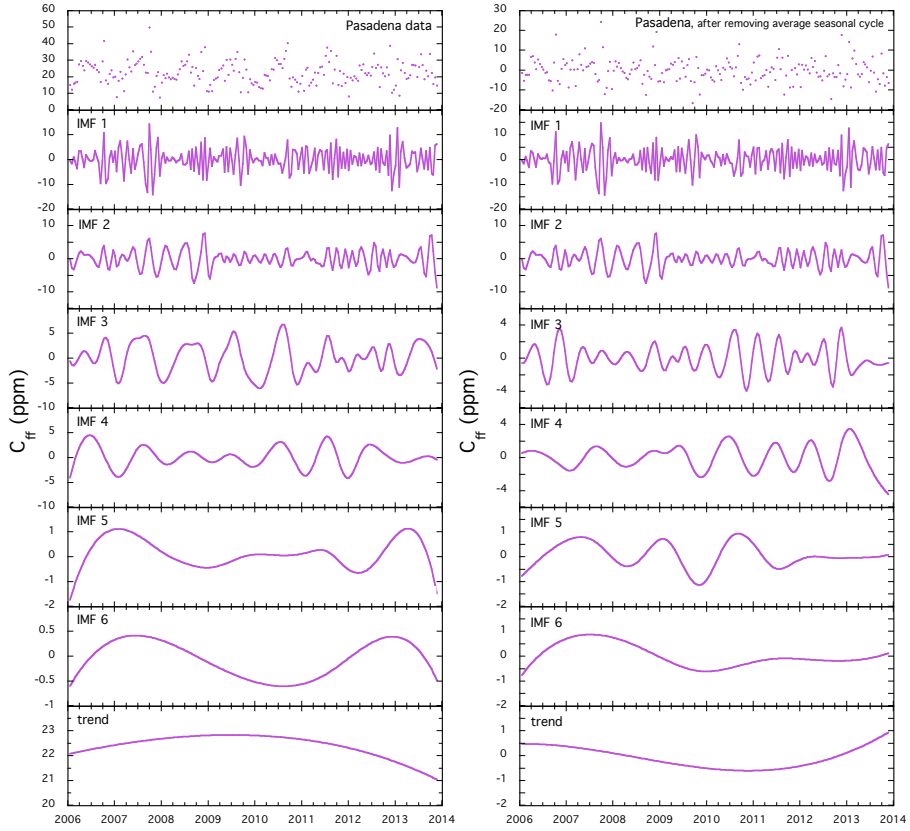

Figure A3. Time series of all of the results from the ensemble empirical mode decomposition (EEMD) analysis of the Pasadena C_{ff}. The left set of panels shows the results for the raw data, whereas the right column shows those for the data after subtraction of the average seasonal cycle. The long-term trend reflecting the economic downturn of the Great Recession is reflected clearly in IMF 6 and the trend of the data after the pronounced seasonality is removed (right-hand column), although there is some evidence of it in IMF 6 of the raw C_{ff} data.

Responses for Referee #1's comments:

Abstract, p. 29593 l.23 The absolute agreement between the bottom up Hestia and top-down approach is not assessed. Therefore, the word "consistent" may be misleading. At some latter point in the manuscript it may be worthwhile to clearly state that emission inventories are not validated absolutely, but only trends (and relative contributions) of bottom-up and top-down approaches are compared.

We have made a minor modification in the title to clarify that this study compares trends in emissions between top-down atmospheric data and bottom-up inventories and data products, not the absolute emissions. The title is now:

Toward consistency between trends in bottom-up CO_2 emissions and top-down atmospheric measurements in the Los Angeles megacity

In the abstract, only variations, seasonality, and trends are discussed. Hopefully, the change in the title will clarify the focus.

p. 29597 l.12 The PDB scale has long been replaced by the VPDB scale and it is recommended to use the VPDB scale.

Thank you for finding this error. It has been corrected, both in the text and in the references.

p. 29597 l.14-17 In this study, an integrated 14C(CO2) sample is obtained by combining 3-7 CO2 samples (afternoon) into one sample. Thus, 14C(CO2) from this integrated sample provides the average fossil fuel CO2 offset. In this manuscript, the monthly-integrated source signature δss is used to obtain a value for δff. However, averaging the source signature δff over time is only valid if δff and δbio do not change over time as otherwise correlation between cff and δff and cbio and δbio can lead to biases (Vardag et al., 2015). As the CO2 samples are always taken during the same (short) time of the day and the integration period is not long, it may be that the effect of the integration is small. However, it might be worthwhile to check and mention this in the manuscript.

This is an interesting point. The Miller-Tans plots suggest that monthly average compositions for δxs are constant, within uncertainty, as indicated by the very high correlation coefficients (Fig. A1). Although this does not guarantee that δff and δbio do not change over time, it does suggest that the system is stable over this time scale. A comment has been added to this effect in Section 2.3.3.

p. 29599 l.20 Please give information on the background Δ14C values such as sampling resolution, precision etc.

The background $\Delta^{14}C$ record at Pt. Barrow, AK is obtained through the UCI/NOAA ESRL (Earth System Research Laboratory) flask network program that collects whole air samples using 6-L, 1-valve stainless steel canisters (Silco Can, Restek Co.) that have been pre-evacuated at UCI. The canisters are pressurized to ~2 atm using an oil-free pump. Two biweekly samples were collected before 2008, and one weekly afterwards. For the period from 17 June 2005 to 17 March 2006, some duplicate samples were collected using 32-L, 1-valve stainless steel canisters. Subsamples were then taken from these samples for ^{14}C analysis. CO_2 is extracted cryogenically at UCI

then converted to graphite by the sealed tube zinc reduction method (Xu et al. 2007). Each sample is ~2.7 mg C in size. Analysis of $\Delta^{14}C$ is performed at the W M Keck AMS facility at UCI with total measurement uncertainty of ±1.3–2.4‰. Mass dependent fractionation is corrected for using "on-line" $\delta^{13}C$ measurements during AMS analysis, which accounts for fractionation that occurred during graphitization and inside the AMS.

Comparison was made over 22 common sample dates spanning 5 yr, differences in measured $\Delta^{14}C$ from Barrow between the UCI and the Scripps Institution of Oceanography's CO_2 Program. It shows differences in measured $\Delta^{14}C$ are consistent with the reported uncertainties and there is no significant bias between the programs (Graven et al., 2013).

The other is the inter-comparison of AMS-based atmospheric $^{14}CO_2$ measurements organized by the NOAA Earth System Research Laboratory, Boulder, Colorado. UCI lab is one the three groups having interlaboratory comparability within 1‰ for ambient level $^{14}CO_2$ (Miller et al. 2013).

This information has been added to Section 2.3.2.

p. 29601 Section 2.3.3. The samples used were all taken during the afternoon hours. However, Miller and Tans (2003) have pointed out that the determination of source signature does not work when CO2 sinks with a different signature than the sources occur. If this is the case in your setting, it may lead to potential biases of the source signature, which should be discussed here.

There are minimal, if any, sinks for CO_2 in this region. The biosphere, as indicated by our data, is not an important player, in general.

p. 29602 l.11 The authors use δbio of -26.6, δng of -40.2 and δpet of -25.5 without stating an uncertainty or typical variation within one year. It should be elaborated how these uncertainties (especially on a seasonal scale) influence the results for cff, cbio, cpet and cng. This should also be included in Fig. 3.

We do not have a measure of the uncertainty for δ_{bio}, although the sensitivity studies of Bakwin et al. (1998) suggest little variation. However, we have analyzed δ_{ng} and δ_{pet} over many years and at different times of year and the standard deviations are ± 0.5 and 1.0 ‰, respectively. We did, in fact, expect a seasonal variation in δ_{pet}, because there are winter and summer blends of gasoline. However, we have observed no significant differences.

p.29606 l.16-22 This section is a bit confusing as the assumption of having no biospheric influence is not correct and also not used in this study. It might be more straightforward to leave this passage out as it seems to be of no use for the reader at this point.

Thank you for pointing this out. This was mentioned above and therefore is redundant here. It has been deleted.

p. 29607 l.5 Throughout the manuscript emission and concentration are used synony-

mously. Without a model, only the contribution of fossil fuel CO2 can be derived but not the fossil fuel CO2 emission. Please correct this in the entire manuscript.

Here and in many other places throughout the manuscript fossil fuel "emissions" has been replaced by C_{ff}.

p. 29608 l.9 Jiang et al. (2012) concluded that the semi-annual oscillation is a consequence of a combination of gross primary production (GPP) and respiration (resp), not net primary production (NPP=GPP+resp) and respiration.

CO_2 semi-annual oscillation is a consequence of a combination of gross primary production and respiration. We have revised this in the main text.

Fig. 11 It might be worthwhile to insert error bars on cpet and cng.

C_{pet} and C_{ng} are now shown as annual averages with standard error bars.

p. 29612 l.2 Could the lag be an artifact of not including seasonal variations of the source signatures (e.g. δbio) into the consideration?

We conclude that the major cause of the seasonal variations is the seasonal shift in wind direction, resulting in a different source region for winter versus summer. None of our information suggests seasonal variations in δbio.

Fig. 12 The uncertainty of cpet should be included in this Figure. Why do EIA and ARB statistics differ by a factor 10^3 ? Please elaborate what "mo" stands for in the unit of [kg CO2/mo] ?

We have the uncertainties plotted in Figure 6 and feel that Figure 12 will be too cluttered if they are included here again. Thanks very much for noticing the error of 10^3 in the units for the EIA data. This has been corrected. [kg CO2/mo] refers to kg CO2 per month. This has been added to the caption.

p.29612 l.20 They agree in the direction of the sub-annual variation, but not in their absolute values.

A phrase has been added to say that they agree in their seasonality.

Fig. 14 Same emission sectors should have the same y-scale so that differences between emission inventories become obvious. This is the case for the green and black axes in Fig 14.

The blue axis is for the LA basin Hestia product, covering a much smaller domain, as does the grey axis, which is for LA and Orange county power plant emissions. The major point being portrayed in this figure is the seasonality. The absolute numbers do not really matter, since the temporal variations are being emphasized.

p.29613 l.6-7 It is interesting that the increase in natural gas consumption is seen earlier in the data than in the emission inventories. If other sectors have not changed significantly (as one might expect?), this might point towards a false emission inventory and might be worth to point out here.

This is a very good point, and we have added a sentence mentioning possible explanations for the different timing. We feel that we cannot suggest a false emission inventory because of the large uncertainties and the lack of atmospheric

modeling here.

p. 29613 l.27 What about long-term changes in source signature of natural gas or petrol? Only if the endmembers of the signature do not change over time it is possible to validate emission inventories as presented here.

We have analyzed natural gas combustion over 30 years and gasoline combustion over 9 years and do not see any significant changes. A comment to this effect has been added in Section 2.3.3.

p. 29615 l.9-14 What are typical uncertainties of the emission inventories used? What are the uncertainties of the top-down approach?

Uncertainties are not given for the bottom-up inventories. We do not produce an emission inventory with our top-down approach. We conclude that we can see a significant 10 % change in C_{ff} using our measurements.

p. 29638 Fig. A3 Please explain why the long-term trend (last row) changes after removing the average (repeated seasonal cycle).

The major reason for the change in the long-term trend between the analysis of the raw values for Cff and those after removing the seasonal cycle is that the uncertainties are overwhelming for the raw data analysis and are much smaller after removing seasonality, which is a common artifact of EEMD known as mode mixing between the dominant mode (i.e. annual cycle in our case) with other modes (e.g. noise). In our case, we can minimize the mode-mixing problem by removing the annual cycle and perform EEMD again. The variations observed are not significant for the raw data analysis, whereas they are for the modified data set. In the revised text:

"Note that there are severe mode mixing problems in IMF3 (e.g. during 2011–2013) between the dominant annual cycle and subseasonal variations, which also affects the nonlinear decompositions in the higher modes. To minimize the effects of mode mixing on the extractions of inter-annual trends, we perform the EEMD again after removing the average annual cycle (minus the mean of the raw data), defined as monthly averages over the entire time period (2006-2013; resulting time series shown in Fig. 10e). The revised inter-annual trend is shown in Fig. 10f."

Technical corrections:

p. 29594 l.13 This is only true in very large cities (Megacities).

We have added the phrase "especially in megacities."

p. 29595 l.27 It is not clear what "all three" refers to here.

We have added a parenthetical remark to explicitly list "all three sources" for clarification.

Response to Referee Jocelyn Turnbull's comments:

Pg 29594 lines 19-20. Indeed bottom-up reporting may not always be reliable, but this comment should be backed up with references, and perhaps more careful phrasing to avoid the implication of finger pointing at "other" countries.

We have changed the wording and added Andres et al. (2012) as a reference.

Pg 29595 lines 1-3. Are there examples outside of the US? Airparif?

There are no examples of such detailed emissions products outside the US of which we are aware.

Pg 29597 lines 18-22. This is an interesting point – what is the optimal number/time length of samples to combine for measurement to give sensible, useful averages? This could be expanded on here or in the results section.

Since all of our samples were aggregated, we have no way to know the optimal number. We see the difference compared with sparser, individual sampling reported by Affek et al. (2006). This is a good study to do in the future, pending funding.

Pg 29597 line 18. Typo – CCAMS.

Good catch, thank you! This has been changed.

Pg 29597 lines 26-27. The CO2 mole fraction error is quite large – I would guess that it is sufficient for this study, but this should be justified.

A comment has been added, explaining that the dominant source of error is from the $\Delta^{14}C$ analyses.

Pg 29598 line 1. How were the 14C errors determined? Is this described in the Xu 2007 paper? Please reference or describe this.

Overall precision is 2‰ which is based on long-term reproducibility of secondary standards. It is described in both Xu et al. 2007 and Xu et al. 2010 papers. Also see the two inter-lab comparisons in the response to Reviewer #1 above.

Pg 29598 lines 23-24. It is a pity there is no more recent La Jolla 14C data.

We agree completely and eagerly hope for funding to continue the analyses.

Pg 29600, lines 9-10. I take it that the nuclear contribution is therefore ignored?

Yes, we have added a comment to this effect.

Pg 29602, line 11. How was the biosphere discrimination determined? The value appears to assume C3 plants, but are C4 plants important in Southern California? Is lawn grass in this area typically C3 or C4? And whether C3 or C4, how certain is this value, and how much seasonal variability might there be? A bias (seasonal or general) in delta-bio would dramatically change the proportions of petroleum and gas determined by this method.

This has been described more thoroughly in the text, in Section 2.3.3. Thank you for raising this important issue. The discussion is as follows:

This value represents data from temperate northern latitudes (28 – 55 °N), dominated

by C3 plants with some C4 grasses present (Bakwin, et al., 1998). Indeed, grasses in southern California are mostly C3 ryes, fescue, and bluegrass, with some C4 grasses such as St. Augustine (www.cropsreview.com/c3-plants.html, last accessed January 25, 2016).

Pg 29603 lines 1-3. This is a reasonably large correction – how large is it relative to the Cbio values themselves? Ie what % of Cbio does it represent?

We have added to the text:

The magnitude of this correction is 0.5 – 1.2 ppm, averaging 0.84 ppm, which represents approximately a quarter of the C_{bio}, but the latter is very small, averaging 3 – 4 ppm and the correction does not affect our results with respect to C_{pet} and C_{ng}.

Section 2.3.4 Time series analysis. The description given here is quite brief, and it is hard to follow the results later. This section could be expanded to clarify what the different IMF categories represent, and how they are determined. See also my comment on the IMF results section.

We have added a description of the algorithm to Section 2.3.4.

Pg 29603 line 23. Bottom-up data products, not inventories – they are based on inventories but are much more complex than that.

We have added "and data products" for clarification.

Pg 29604 lines 23-24. How does the fraction of Cbio change through the seasons? This is discussed in a later section, but you could refer to that section here, since it is an obvious question when reading this section.

We have added a reference to the later section.

Pg 29606. See my previous comment about the delta-bio for C3 vs C4 plants. How would the interpretation here change if delta-bio was strongly influenced by C4 plants?

We have added a few sentences of discussion, saying that more influence by C4 plants would raise the C_{ng} curve relative to C_{pet}, because C4 plants discriminate less strongly against the heavy isotope of carbon.

Pg 29607. Thanks for the nice discussion of the percentages from the biosphere. Does the larger fraction and larger overall magnitude of bio emissions during the cooler months imply a larger biosphere flux during the cooler months? This would be worth a few sentences of discussion.

We have added two sentences of discussion to Section 3.2. We do not try to interpret the biosphere signal here, because it is very small relative to the uncertainties.

Pg 29608 line 2. r2 should be lower case.

Changed!

Pg 29608 lines 9-14. This is hard to follow without thoroughly reading the Jiang paper. Please clarify why the semi-annual oscillation might be driven by NPP and respiration.

In the winter season, photosynthesis is largely reduced. The peak for gross primary

production is relatively flat in winter. However, there are still CO_2 emitted to the atmosphere by respirations from the biosphere in winter, which has a relatively sharp peak compared with the photosynthesis term. The combination of gross primary production and respiration leads to the double peaks in each year in the net ecosystem production, which contributes to the semi-annual oscillation in CO_2 [Jiang et al., 2012]. We have revised this is Section 3.3.

Pg 29609 lines 7-8. Why would artificial irrigation reduce the biosphere signal? Intuition would suggest an opposite effect. Please expand and reference to clarify.

We have added a comment saying that we suggest that artificial irrigation removes the seasonality that might be expected for wet versus dry seasons.

Section 3.4.1. The methodological basis for this section is not very clearly explained either in the text or the figure caption. The IMFs are sometimes referred to as "IMF 1", "IMF 2", etc., and sometimes by names that reflect what the IMF might represent, e.g. "annual cycle", etc. It is not always obvious which IMF number relates to which cycle. A more detailed introduction to the method would be very helpful, perhaps in the methods section of the paper. How many IMF modes were identified? Why is the trend+IMF6 such an important curve – what is significant about IMF6 versus the other IMF modes?

The goal of this analysis is to get at the longer-term trend, which requires removing high-frequency noise and signals for which we understand the governing process. We understand the annual cycle and wish to isolate the longer-term signal. A description of the process for calculating the modes is given in Section 2.3.4. The full set of IMFs is given in Figure A3.

Pg 29610 lines 7-10. Figure 10f is the detrended signal, and is just showing the deviations from the mean, correct? It is a bit hard to follow where the 7.3 ppm standard deviation comes from when referring to this figure.

This standard deviation comes from the raw data set, since the set without the annual cycle is simply an arithmetic manipulation of the original data. Figure 10f is the sum of the final trend (only one maximum or minimum) plus IMF 6 for the data set that has had the average seasonal cycle removed. It has not had any other trend, such as linear, removed. Therefore is contains information about variations that are inter-annual.

Lines 8-13. Again, it is hard to follow how the 9.5% change is determined. Perhaps a version of figure 10f that is adjusted with a mean value matching that of the actual data and the deviations around that mean, rather than just showing the deviations from the mean would help.

We have changed the plots of the modified data set, seasonal cycle removed, to include the average of the raw data. This leads to deleting the confusing parenthetical remarks in the discussion. Thank you for pointing this out.

Lines 25-30. This is an interesting discussion about how Cff decreases might not follow economic changes perfectly, but I am not convinced that such a detailed comparison is justified by the data presented here. First, there are fairly large error bars on the Cff changes shown in figure 10f, so a decrease of 13% might be consistent with the data.

Second, the analysis makes no attempt to account for interannual variability in meteorology, which could potentially drive the observed changes.

We have deleted this discussion, since it does over interpret the data.

Pg 29611 lines 11-15. The shape of the Cff decrease appears to be different between the observations and the CARB inventory. CARB shows a minimum in 2011/2012, whereas the observations as shown in figure 10f appear to show a minimum in 2010. How can these be reconciled?

A comment has been added to address this:

There is a difference in timing between the data presented here (2010) and those from the CARB inventory (2011-2012). The difference may be due to uncertainties in the data or to the different domains covered by the two data sets.

Pg 29611, lines 23- 30 and onto the following page. Again, how would uncertainty in delta-bio influence these conclusions? A short lag between gasoline purchase and combustion makes sense, but it is hard to believe there is a 3 month lag, given that most people fill up their vehicles every week or two. What other possible explanations are there for this lag?

As mentioned above, more influence from C4 plants would raise the C_{ng} curve relative to the C_{pet} curve.

We suggest that the different domains of our data and the CARB and EIA inventories are the dominant reason for the difference in seasonality. The statement regarding lag between purchase and combustion has been deleted.

Figure 11. The presentation of this figure could be improved. The thick lines (representing the CARB inventory data) draw the eye, and give the impression that they represent some sort of smoothed average of the observational data. Yet no smoothed average of the observational data is actually given on this figure. Perhaps fits to the observational data could be added so that a more direct comparison could be made.

We have changed this figure to use the annual averages from the Pasadena data as compared with the annual CARB inventory.