

Isotopic measurements of atmospheric methane in Los Angeles, California, USA: Influence of “fugitive” fossil fuel emissions

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[1] Recent studies have suggested that CH₄ emissions in Los Angeles and other large cities may be underestimated. We utilized stable isotopes (¹³C and D) and radiocarbon (¹⁴C) to investigate sources of CH₄ in Los Angeles, California. First, we made measurements of $\delta^{13}\text{C}$ and δD of various CH₄ sources in urban areas. Fossil fuel CH₄ sources (oil refineries, power plants, traffic, and oil drilling fields) had $\delta^{13}\text{C}$ values between -45 and -30‰ and δD values between -275 and -100‰ , whereas biological CH₄ (cows, biofuels, landfills, sewage treatment plants, and cattle feedlots) had $\delta^{13}\text{C}$ values between -65 and -45‰ and δD values between -350 and -275‰ . We made high-altitude observations of CH₄ concentration using continuous tunable laser spectroscopy measurements combined with isotope analyses (¹³C, ¹⁴C, and D) of discrete samples to constrain urban CH₄ sources. Our data indicate that the dominant source of CH₄ in Los Angeles has a $\delta^{13}\text{C}$ value of approximately -41.5‰ and a δD value between -229 and -208‰ . $\Delta^{14}\text{C}$ of CH₄ in urban air samples ranged from $+262$ to $+344\text{‰}$ (127.1 to 134.9 pMC), depleted with respect to average global background CH₄. We conclude that the major source of CH₄ in Los Angeles is leakage of fossil fuels, such as from geologic formations, natural gas pipelines, oil refining, and/or power plants. More research is needed to constrain fluxes of CH₄ from natural gas distribution and refining, as this flux may increase with greater reliance on natural gas and biogas for energy needs.

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1. Introduction

[2] Anthropogenic activities have resulted in increasing levels of greenhouse gases, including methane (CH₄), with current atmospheric mixing ratios that have approximately doubled over the past 200 years [Sowers *et al.*, 2005; MacFarling Meure *et al.*, 2006; Mitchell *et al.*, 2011]. Methane has a global warming potential of about 25 times that of carbon dioxide (CO₂) on a 100 year time scale [Forster *et al.*, 2007]. Major global sources of CH₄ include wetlands, cattle and other ruminant animal ranching, fires, and rice paddies, but CH₄ is also released from landfills and

wastewater treatment plants, and during fossil fuel mining and distribution [Cicerone and Oremland, 1988; Reeburgh, 2004]. Methane is also an important component in the overall oxidative capacity of the troposphere, as it is consumed by reaction with atmospheric radicals [Cicerone and Oremland, 1988].

[3] Stable isotopes and radiocarbon have been previously employed to determine sources of both CO₂ [e.g., Pataki *et al.*, 2003a; Fisher *et al.*, 2006; Djuricin *et al.*, 2010] and CH₄ [Cicerone and Oremland, 1988; Bergamaschi *et al.*, 1998; Kessler *et al.*, 2008; Lowry *et al.*, 2001, 2009; Kai *et al.*, 2011]. For CH₄, $\delta^{13}\text{C}$ and δD ratios can be used to differentiate microbial from thermogenic sources. Microbial CH₄ is characterized by $\delta^{13}\text{C}$ values of between -50‰ and -110‰ and δD values of -150‰ to -400‰ [Cicerone and Oremland, 1988; Quay *et al.*, 1991, 1999; Whiticar and Schaefer, 2007]. Thermogenic CH₄ (generated at high temperature in the Earth’s crust, as in fossil fuels) has $\delta^{13}\text{C}$ values between -45‰ and -20‰ , and δD values between -100‰ and -275‰ [Whiticar and Schaefer, 2007]. Consumption of CH₄ by methanogenic bacteria or by oxidation with atmospheric radicals generally causes enrichment in both $\delta^{13}\text{C}$ and δD of remaining CH₄ [Tyler, 1986; Whiticar, 1999; Saueressig *et al.*, 1996, 2001; Snover and Quay,

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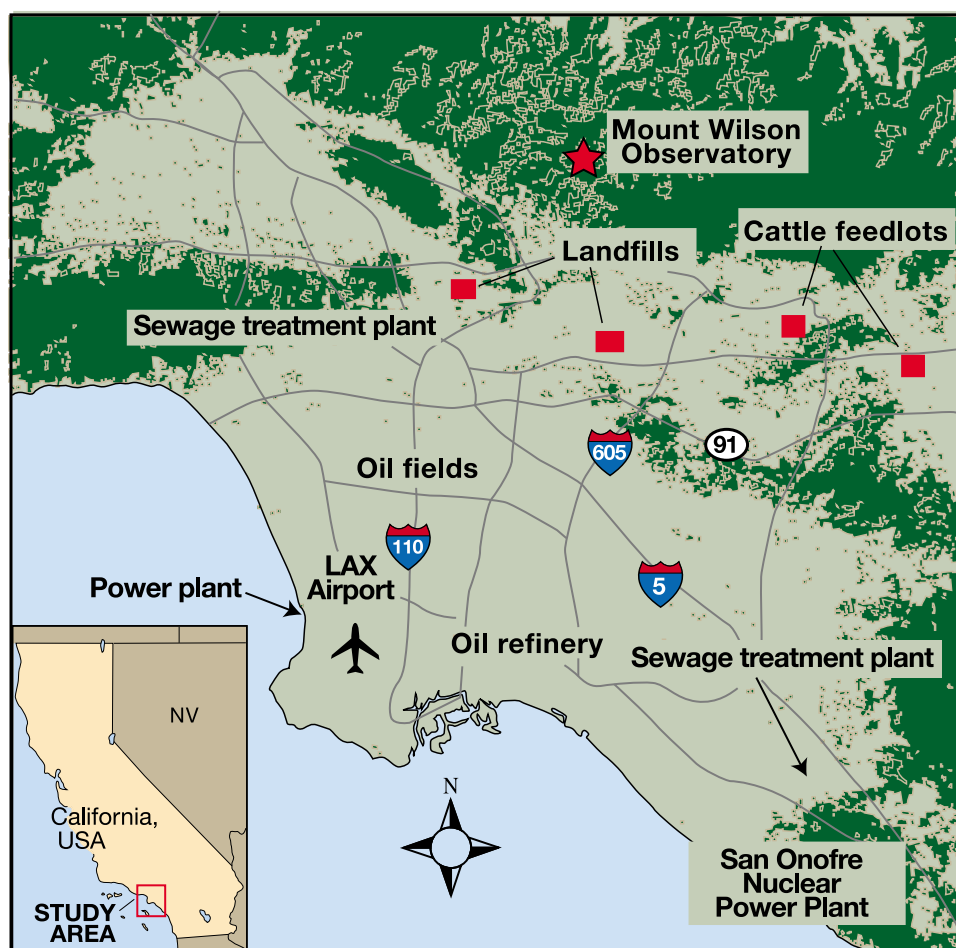


Figure 1. Map of the study area, including point source sampling sites and high-altitude monitoring site (Mount Wilson Observatory, 1707 m above sea level). Dark green areas represent mountainous areas, and light green areas are low-lying urbanized areas.

2000]. Radiocarbon content may be a particularly good indicator of CH_4 source, since most fossil CH_4 sources are nearly 100% depleted in ^{14}C [Quay *et al.*, 1999; Lassey *et al.*, 2007a, 2007b; Kessler *et al.*, 2008; Pohlman *et al.*, 2009; O'Sullivan *et al.*, 2010]. In contrast, other sources of methane have ^{14}C contents that are approximately modern, including rice paddies [Nakagawa *et al.*, 2002], landfills [Coleman *et al.*, 1995], sewage treatment plants [O'Sullivan *et al.*, 2010] and cattle [Johnson and Johnson, 1995]. It is important to note that nuclear power plants and nuclear waste sites emit $^{14}\text{CH}_4$ without a significant flux of CH_4 overall, leading to global background $\Delta^{14}\text{C}$ of CH_4 values that are more enriched than atmospheric CO_2 [Lassey *et al.*, 2007a, 2007b], although measurements are sparse due to large sample volume requirements and the high cost of radiocarbon dating.

[4] While the global emissions of CH_4 are relatively well constrained, regional emissions and the contribution of individual sources to these emissions is not [Bergamaschi *et al.*, 2010; Dlugokencky *et al.*, 2011]. In particular, relative proportion of urban greenhouse gas sources may differ from the magnitude of global sources, which complicates the use of global models for regional source estimation [Townsend-Small *et al.*, 2011a, 2011b]. For example, studies

of tropospheric air in Los Angeles have found that CH_4 concentrations are larger than predicted by statewide models [Wunch *et al.*, 2009; Hsu *et al.*, 2010], indicating that some emissions factors for urban areas are missing or underestimated. Studies of CH_4 emissions in urban Indianapolis, USA, also showed evidence for significant urban CH_4 sources that are not accounted for in greenhouse gas emissions models [Mays *et al.*, 2009]. Studies of CH_4 concentrations in St. Petersburg, Russia showed evidence for significant urban emissions, estimated at about 100 kT yr^{-1} [Nisbet, 2005].

[5] A few prior studies have employed stable isotope analyses to determine sources of urban CH_4 and have shown that either landfills or natural gas leaks are significant in urban areas. In Krakow, Poland, analyses of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of CH_4 showed that natural gas leaking was the dominant source of anthropogenic CH_4 in that city [Kuc *et al.*, 2003; Nisbet, 2005]. In London, UK, $\delta^{13}\text{C}$ analyses showed that the dominant sources of CH_4 in the urban area were landfills (~80% of total source) and natural gas distribution systems (~20%) [Lowry *et al.*, 2001; Fisher *et al.*, 2006].

[6] The objective of this study was to determine whether isotopes could be useful tracers of urban versus natural or agricultural CH_4 sources in southern California. We also

Table 1. Data for Samples Collected for Point Source Determination, Including Sampling Location and Date, CH₄ Concentration, and $\delta^{13}\text{C}$ and δD (Where Applicable)^a

Sample Number	Sample Type	Location	Date ^b	CH ₄	$\delta^{13}\text{C}\text{-CH}_4$ (‰)	$\delta\text{D}\text{-CH}_4$ (‰)
S1	Traffic	LAX parking garage	5/12/08	1.85 ppm	−30.4	−130.1
S2	Traffic	Sepulveda tunnel	5/12/08	1.87 ppm	−30.2	−113.2
S3	Oil field	Oil drilling rig, Kenneth Hahn Park, Culver City	5/12/08	2.27 ppm	−41.7	−190.4
S4	Power plant	Coastal power plant, Redondo Beach	5/12/08	1.86 ppm	−39.6	−192.0
S5	Oil refinery	Torrance, Los Angeles County	5/12/08	5.31 ppm	−44.7	−277.2
S6	Oil refinery	Carson, Los Angeles County	5/12/08	1.87 ppm	−44.7	−249.0
S7	Landfill biofuel	Los Angeles County landfill, from gas collection stream	11/29/07	~30%	−61.5	−316.1
S8	Landfill biofuel	Los Angeles County landfill, from gas collection stream	11/29/07	~30%	−61.9	−313.9
S9	Manure biofuel	Manure digester test facility, Riverside County	6/28/07	2.24 ppm	−50.5	−280.0
S10	Manure biofuel	Manure digester test facility, Riverside County	6/28/07	2.57 ppm	−50.7	−296.3
S11	Manure biofuel	Manure digester test facility, Riverside County	6/28/07	15.53 ppm	−52.4	−333.6
S12	Manure biofuel	Manure digester test facility, Riverside County	6/28/07	4.04 ppm	−50.2	−317.0
S13	Sewage treatment plant	Orange County	11/9/07	3.32 ppm	−46.3	−298.0
S14	Sewage treatment plant	Los Angeles County	11/2/07	3.11 ppm	−47.0	n.m.
S15	Cow manure	Commercial dairy farm, Riverside County	11/7/07	2.36 ppm	−59.1	−348.8
S16	Cow manure	Commercial dairy farm, Riverside County	11/7/07	3.18 ppm	−59.4	−338.4
S17	Cow manure	Commercial dairy farm, Riverside County	11/7/07	46.28 ppm	−62.1	n.m.
S18	Cow breath	Commercial dairy farm, Riverside County	11/7/07	132.33 ppm	−65.0	n.m.
S19	Cow breath	Commercial dairy farm, Riverside County	11/7/07	76.08 ppm	−60.2	n.m.
S20	Cow breath	Commercial dairy farm, Riverside County	11/7/07	90.97 ppm	−64.6	n.m.

^aData corrected for the presence of background air, as described in the text; n.m. denotes not measured.^bDate format is month/day/year.

hoped to use stable isotopes as well as radiocarbon to make preliminary estimates of the dominant source of CH₄ in the metropolitan area of Los Angeles, California.

2. Methods

2.1. Study Area

[7] Los Angeles is one of world's "megacities" with an estimated population of up to 15 million in the metropolitan area, which includes parts of Los Angeles, Orange, Riverside, and San Bernardino counties. The city is constrained by peninsular and transverse mountain ranges with dominant onshore winds (Figure 1), except during occasional wind reversals: the "Santa Ana" winds. This commonly results in atmospheric temperature inversions in the late afternoon that create notorious smog events. In general, wind trajectories are from the ocean to the land during the day, and in the opposite direction in the afternoon, with stronger sea breezes in summer than in winter [Turpin and Huntzicker, 1991]. The climate is semiarid/Mediterranean with most rain events occurring during only a few days during winter.

2.2. Sample Collection

[8] There were two components of our field sampling campaign: (1) point source identification and sampling around the basin followed by (2) observation and measurement of

CH₄ concentrations and isotope ratios in urban air sampled at high altitude. For part 1, we sampled a range of potential CH₄ sources including fossil fuel sources (oil wells, power plants, oil refinery, and vehicle emissions) as well as biogenic sources (cow breath, landfills, biofuels (from both manure and landfill sources), and sewage treatment plants). These samples were collected from November 2007 to May 2008. All samples were collected using a battery-powered oil-free GAST diaphragm pump through a magnesium perchlorate water trap in preevacuated stainless steel gas canisters ranging in size from 2 to 6 L. The typical flow rate during sampling was about 1.5 L min^{−1} and canisters were filled to approximately 2 atm.

[9] Sampling locations and dates are shown in Tables 1 and 2. Samples of vehicle emissions were taken in the vicinity of downtown LA traffic (S1 and S2, Table 1). Oil field, oil refinery, and power plant samples (S3–S6, Table 1) were taken as close as possible to the source, using a hand-held anemometer to ensure that wind was blowing from the source to the sample collection device. Biofuel samples (S8–S12, Table 1) were collected from or near collection systems at biofuel generation plants. Sewage treatment plant air was sampled from just above the surface of the treatment tanks, within the freeboard space to avoid sampling large amounts of background air (S13 and S14, Table 1). Samples from cattle farms (S15–S20, Table 1) were collected in two ways:

Table 2. Additional Measurements of CH₄ in Air Samples From Around Los Angeles Not Associated With a Specific Point Source and Measured for $\delta^{13}\text{C}$ Only^a

Sample Type	Location	Date ^b	CH ₄ (ppm)	$\delta^{13}\text{C}\text{-CH}_4$
City air: freeway traffic	I-5 at 60 freeway	3/6/08	2.03	−46.39
City air: freeway traffic	I-5 at Dodger Stadium	3/6/08	1.98	−46.32
City air: freeway traffic	I-5 at Atlantic Blvd.	3/6/08	2.06	−46.24
City air: freeway traffic	Intersection of I-605, I-5, and I-405	3/6/08	2.03	−46.55
City air: freeway traffic	I-405 at Century Blvd.	11/2/07	2.62	−44.91
City air: near sewage treatment plant/prison	Terminal Island, near Long Beach/San Pedro harbor	5/12/08	1.83	−37.10

^aThese data are not corrected for the presence of background air.^bDate format is month/day/year.

(1) using flux chambers placed over cow fields covered in manure and (2) by holding the sample collection line up to each cow's mouth. Finally, we sampled air around the city for preliminary characterization of CH₄ composition in urban air. These samples are shown in Table 2. Freeway traffic samples were collected from out the window of a car stuck in traffic, and samples from near the Terminal Island treatment plant and prison were collected from the side of the road.

[10] Part two of the study was conducted in August 2009, at the Mount Wilson Observatory, located in the mountains directly east of Los Angeles (Angeles National Forest; 34°13'25" N; 118°03'42" W; 1707 m above sea level). We installed a thermoelectrically cooled interband cascade tunable laser spectroscopy (TLS) instrument [Christensen *et al.*, 2010] for real-time detection of CH₄ concentrations at the weather station operated by the California Laboratory for Atmospheric Remote Sensing (<http://clarweather.jpl.nasa.gov/>). The TLS made six CH₄ concentration measurements per minute, with a scan-to-scan fluctuation of about 30 ppbv [Christensen *et al.*, 2010]. We also collected discrete samples of air at regular intervals and over a range of CH₄ concentrations for later analysis of $\delta^{13}\text{C}$, δD , and $\Delta^{14}\text{C}$ of CH₄. Samples were collected through a magnesium perchlorate water trap in 32 L stainless steel gas canisters at up to 3 atm, for a total sample volume of approximately 100 L. Samples were collected using a GAST oil-free diaphragm pump operating at about 6 L min⁻¹, so samples represent air collected over about a 15 min period.

2.3. Sample Analysis

[11] Methane concentration was measured on a Shimadzu Scientific Instruments GC-14A gas chromatograph with flame ionization detector (GC-FID). Sample concentrations were referenced to a gas standard (1.903 ppm CH₄) that has been intercompared to NOAA Global Monitoring Division reference standards (CMDL83 scale [Lang *et al.*, 1990]). The precision of this measurement is ± 5 to 10 ppb, or about 0.25 to 0.50% uncertainty.

[12] Stable isotope ratios were analyzed at the University of California, Irvine using continuous flow isotope ratio mass spectrometry according to the method of Rice *et al.* [2001], with combustion to CO₂ for $\delta^{13}\text{C}$ and pyrolysis to H₂ for δD . Carbon and hydrogen stable isotope ratios are expressed in delta (δ) notation, where the ratio of the rare to abundant isotope is expressed relative to an internationally recognized standard (Pee Dee Belemnite (PDB) and Vienna Standard Mean Ocean Water (VSMOW), respectively). The uncertainties of $\delta^{13}\text{C}$ and δD measurements have been estimated at 0.05‰ and 1.1‰, respectively. Extended details about calibration standards for $\delta^{13}\text{C}$ and δD are included in the work by Tyler *et al.* [2007]. Isotope ratios of source signatures (shown in Figure 2 and Table 1) are corrected for the average background concentration and isotope ratio of atmospheric methane using the following equation:

$$\begin{aligned}
 (\text{total } \delta) * (\text{total CH}_4 \text{ concentration}) &= (\text{source } \delta \text{ signature}) \\
 &* (\text{source CH}_4 \text{ concentration}) + (\text{background } \delta) \\
 &* (\text{background CH}_4 \text{ concentration}).
 \end{aligned}$$

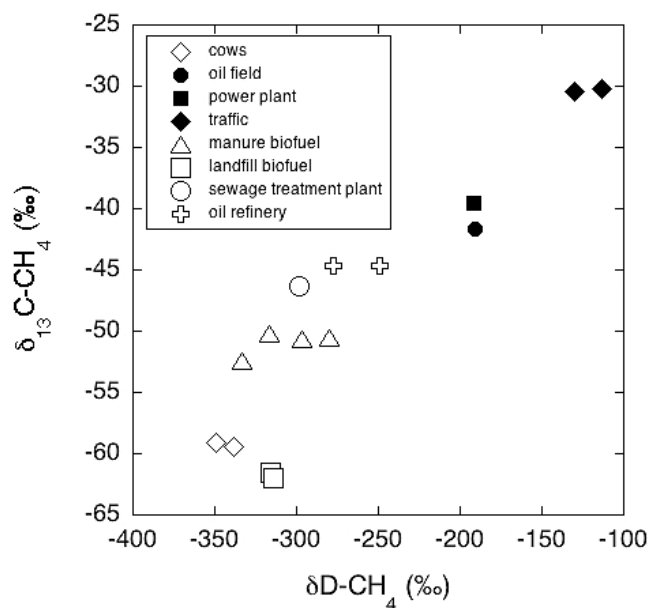


Figure 2. Carbon and hydrogen stable isotopic composition of methane collected from various sources in southern California. Solid symbols represent fossil-derived CH₄, and open symbols represent biological sources. Isotope ratios represent source signatures corrected for the presence of background air.

[13] “Background” CH₄ concentration and isotope composition is usually determined from remote “clean air” sites and is variable with season, latitude, and altitude [Quay *et al.*, 1991, 1999; Tyler *et al.*, 1999, 2007; Miller *et al.*, 2002]. For calculating source signatures of CH₄ in this study, we used data from the same month collected at the Montana de Oro site, located north of Los Angeles and outside of significant urban influence. These data are presented by Tyler *et al.* [2007]. In order to determine the source of excess CH₄ for samples collected from air at the Mount Wilson Observatory, we constructed plots of isotope composition versus the inverse of CH₄ concentration, or Keeling plots [Keeling, 1958, 1961; Pataki *et al.*, 2003b].

[14] Air samples for analysis of $\Delta^{14}\text{C}$ of CH₄ were purified by vacuum line to remove CO₂ and CO, combusted to convert CH₄ to CO₂, graphitized using H₂ reduction, and analyzed for $\Delta^{14}\text{C}$ by accelerator mass spectrometry (AMS) at the Keck Carbon Cycle AMS Facility at the University of California, Irvine [Beverly *et al.*, 2010]. The precision of this method is usually 2 to 3 ‰ for normal, 1 mg C, modern samples, based on long-term quality control secondary standards. However, since our CH₄ sample sizes were so small (0.05 – 0.12 mg C), the relative error ranged from ± 4 to 10‰ after propagating the errors involved in background corrections, and precision generally varied with sample size (Table 3). Radiocarbon concentrations are presented as percent of the Modern carbon standard (pMC) and as $\Delta^{14}\text{C}$ following the conventions of Stuiver and Polach [1977]. Sample preparation backgrounds have been subtracted based on measurements of ¹⁴C-free CO₂ from coal, and data are

Table 3. Methane Concentrations and Isotope Composition for Los Angeles Air Collected at the Mount Wilson Observatory^a

Sample Number	Date and Time ^b	CH ₄ (ppm)	$\delta^{13}\text{C}$ (‰)	δD (‰)	$\Delta^{14}\text{C}$ (‰)	pMC
1	8/4/09 11:27	1.76	−47.81	−93.2	261.9 ± 6.7	127.09 ± 0.0067
2	8/4/09 13:50	2.06	−47.79	−107.8	293.7 ± 5.7	130.30 ± 0.0057
3	8/4/09 15:07	2.02	−46.94	−103.7	270.1 ± 5.2	127.92 ± 0.0052
4	8/4/09 17:19	1.80			333.7 ± 11.5	134.32 ± 0.0115
5	8/4/09 21:01	1.76	−47.13	−87.6		
6	8/5/09 01:18	1.76	−47.11	−85.1		
7	8/5/09 05:46	1.76			339.8 ± 10.9	134.94 ± 0.0109
8	8/5/09 11:18	1.84	−47.13	−90.6	344.3 ± 5.9	135.39 ± 0.0059
9	8/5/09 13:54	1.94	−46.58	−99.7		
10	8/5/09 14:43	1.89	−46.96	−94.7		
11	8/5/09 15:45	1.79	−47.24	−88.7		
12	8/5/09 17:35	1.83	−47.14	−93.3		

^aData in Figures 2 and 3.^bDate format is month/day/year.

corrected for isotope fractionation to −25‰ using the online $\delta^{13}\text{C}$ values measured by the AMS.

3. Results

3.1. Stable Isotope Composition of CH₄ From Urban Sources

[15] Results for point source measurements of CH₄ concentration, $\delta^{13}\text{C}$, and δD are shown in Table 1 and Figure 2. Figure 2 shows the background-corrected source signature values of $\delta^{13}\text{C}$ and δD for CH₄ sampled in the Los Angeles basin. Fossil fuel CH₄ (solid symbols in Figure 2) was enriched in ^{13}C and D, whereas biological sources were more depleted in both isotopes (open symbols in Figure 2). We also measured some additional CH₄ from point sources in Los Angeles for $\delta^{13}\text{C}$ only (Table 1). Fossil fuel derived samples had $\delta^{13}\text{C}$ values above −45‰ and δD values above about −275‰ (Figure 2). Biological samples had $\delta^{13}\text{C}$ values below about −50‰ and δD below −275‰. In general, separation between fossil and biological CH₄ was better for $\delta^{13}\text{C}$ than for δD (Figure 2). Sewage treatment plant samples were intermediate between the two types of sources (Figure 2 and Table 1). Samples taken in enclosed parking garages and traffic tunnels had very enriched $\delta^{13}\text{C}$ and δD values, at the high end of our measurement range, similar to previous studies [Nakagawa *et al.*, 2005]. Some point source isotope values were derived from relatively small enrichments in CH₄ concentrations, which may increase uncertainty (see Table 1).

3.2. Isotopic Composition of CH₄ in Urban Air

[16] There was a good correlation between CH₄ concentration measurements by the TLS instrument and in discrete samples measured by GC-FID (Figure 3a; $r^2 = 0.975$, $p < 0.0001$). Both 4 and 5 August showed similar meteorological conditions and trends in CH₄ concentrations, with peak CH₄ concentrations occurring in the midafternoon, and near-background air observed at other times (Figure 3). In general, wind in the Los Angeles basin is onshore, and the study period was no exception. During the night and early morning, the Mount Wilson site was located within the planetary boundary layer, characterized by background CH₄ concentrations and dry conditions (see H₂O vapor and wind direction data presented by Christensen *et al.* [2010]). As is usual in the region, in the early afternoon, onshore breezes

and temperature increases forced air from offshore and through the city up to the field station for a period of about 3 or 4 h, before cleaner, inland air from the Mojave desert pushed the CH₄-enriched air away (Figure 3) [Turpin and Huntzicker, 1991]. This pattern of urban air rising above and over the San Gabriel mountains in late afternoon has previously been shown for CH₄ and other air constituents in Los Angeles [Hsu *et al.*, 2010; Langford *et al.*, 2010].

[17] On both 4 and 5 August, the increase in CH₄ concentration was accompanied by an increase in $\delta^{13}\text{C}$ of up to 1‰ and a decrease in δD of 15–20‰ (Figures 3b and 3c). On both 4 and 5 August, there was a linear relationship between δD and the inverse of CH₄ concentration with a y intercept between −203‰ and −228‰ (\pm approximately 1‰, the error of the δD measurement) (Figure 4b), indicating that excess CH₄ was derived from a fossil fuel source (Figure 2). There was a significant relationship between $\delta^{13}\text{C}$ and the inverse of CH₄ concentration on 5 August (Figure 4a), with a y intercept of −41.5‰. This intercept falls into the range of fossil fuel-derived CH₄ shown in Figure 2. On 4 August, there was no relationship between $\delta^{13}\text{C}$ and $1/\text{CH}_4$. This is due to two apparent outliers (Samples 1 and 2, Table 3) whose $\delta^{13}\text{C}$ values do not scale with δD or CH₄ concentration. The source of this variability is unknown, and outlier sample $\delta^{13}\text{C}$ values were reanalyzed with the same result.

[18] There was no relationship between CH₄ concentration and $\Delta^{14}\text{C}$, and $\Delta^{14}\text{C}$ ranged from +262‰ to +344‰ (127.1 to 134.9 pMC; Figure 3d). The ^{14}C content of CH₄ in our two background air samples (1.76 ppm CH₄) ranged from +262‰ to +340‰, almost encompassing the entire range of $\Delta^{14}\text{C}$ across the concentration gradient.

4. Discussion

4.1. Isotopic Composition of Point Source CH₄

[19] Measurements of fossil fuel and biological CH₄ sources in the Los Angeles generally agree with previous work showing that fossil sources are more enriched in both ^{13}C and D than biological sources [Cicerone and Oremland, 1988; Whiticar, 1999]. We also provide some new information on emerging urban CH₄ sources, including the stable isotope composition of CH₄ of biofuels (from both landfills and manure) and sewage treatment plants.

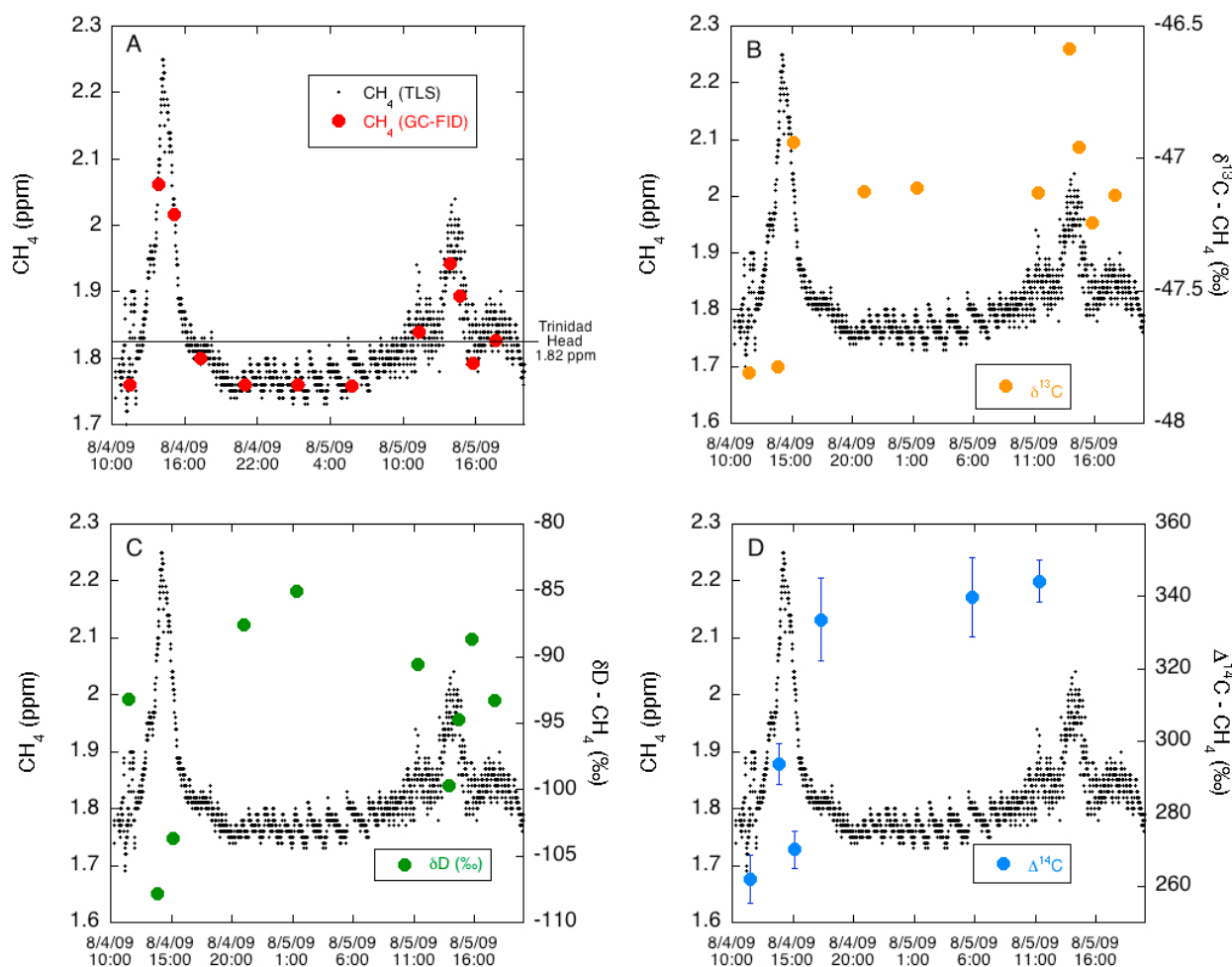


Figure 3. (a) Methane concentrations in air observed at Mount Wilson Observatory as measured continuously with TLS (black dotted line) and in discrete samples with GC-FID (red points). Also shown is the approximate concentration of CH_4 in unpolluted air (1.82 ppm) as measured at Trinidad Head, California, by the NOAA flask sampling network. Shown are (b) $\delta^{13}\text{C}$, (c) δD , and (d) $\Delta^{14}\text{C}$ in discrete samples, shown with CH_4 concentrations measured by TLS. Data for discrete samples shown in Table 3.

[20] Biofuels are likely to encompass a larger portion of southern California's energy portfolio as fossil fuel prices rise and as the state enforces greenhouse gas emissions limits. Interestingly, we found large differences in $\delta^{13}\text{C}$ in two types of biofuels (landfill (−61‰) and manure (−51‰)), but similar δD values (−280 to −330‰) (Figure 2). At the (closed) landfills we sampled, CH_4 is extracted by pumping through a network of pipelines. In general in California, closed landfills are managed in this way to provide fuel for trash collection vehicles. We sampled landfill biofuel (about 30% CH_4) directly from this system. The vacuum system likely prevents consumption of CH_4 by soil microbes in upper layers of the landfill. Previous analyses of $\delta^{13}\text{C}$ of CH_4 from diffuse landfill emissions are more enriched than our landfill biofuel measurements, likely due to CH_4 oxidation in cover soils [Chanton *et al.*, 1999, 2008]. Biofuels derived from cow manure, however, are more enriched in ^{13}C and, to a lesser degree D, than CH_4 measured on cattle feedlots (Figure 2 and Table 1). The manure biofuel test facility we visited was an anaerobic digester supplied with manure from off-site facilities, and

relies on increased microbial activity in the digester to create greater CH_4 production than at feedlots, with increased enrichment in stable isotope composition.

[21] Our data show that sewage treatment plants in the Los Angeles area emit CH_4 (Table 1), and we have previously shown that these systems are a large source of N_2O in the region [Townsend-Small *et al.*, 2011b]. In water recycling systems where denitrification is enhanced, CH_4 may be emitted as a by-product of low oxygen conditions. Only a handful of previous studies have analyzed the isotopic composition of CH_4 derived from sewage treatment. In a nitrification-denitrification plant in Japan, Toyoda *et al.* [2011] found CH_4 emissions of $14.1 \text{ mg CH}_4 \text{ m}^{-3}$, with a $\delta^{13}\text{C}$ signature of −50.7‰, depleted with respect to background air. Methane emissions from sludge digester-type treatment plants may be even higher, but we do not know the isotopic composition of such CH_4 . No previous study has measured the δD of CH_4 from sewage treatment plants, but this is deserving of future research, as our preliminary data show that this source may be isotopically distinct from biological and fossil fuel sources. A better understanding of the

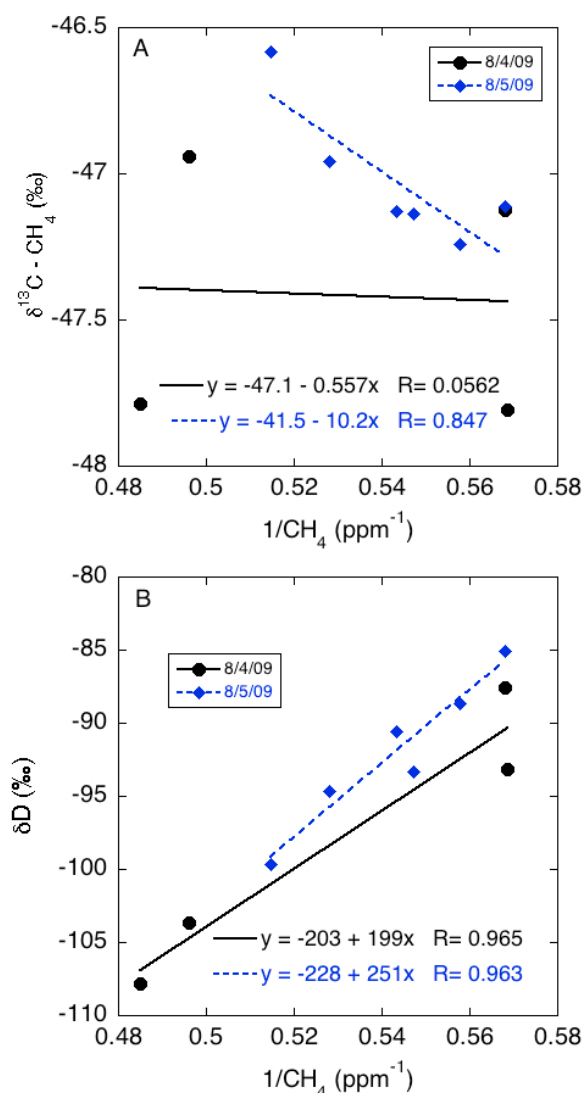


Figure 4. Keeling plots of $1/\text{CH}_4$ concentration versus (a) $\delta^{13}\text{C}-\text{CH}_4$ and (b) $\delta\text{D}-\text{CH}_4$.

CH_4 flux from sewage treatment in this region is also needed, as wastewater recycling is an important component of the water management portfolio in arid southern California.

[22] There is a small but increasing amount of evidence that C in wastewater treatment plants is not entirely modern, either because of fossil C in detergents and pharmaceuticals [Griffith *et al.*, 2009], or due to methanol added to support denitrification [Townsend-Small *et al.*, 2011b]. One study in Japan found dissolved organic C in sewage treatment plants with ^{14}C ages up to 5000 years old [Nara *et al.*, 2010], and rivers in northern California have dissolved organic C with low radiocarbon content, perhaps due to the presence of wastewater in urban rivers [Sickman *et al.*, 2010]. We did not make direct measurements of $\Delta^{14}\text{C}$ of CH_4 from wastewater treatment plants in the area, but we have found that CO_2 sampled from wastewater treatment tanks contains up to 10% fossil carbon (X. Xu, unpublished data, 2010). This is an important area of future study, as wastewater

treatment may contribute greater greenhouse gas emissions as global development increases.

4.2. Isotopic Constraints on Sources of CH_4 in Los Angeles

4.2.1. Stable Isotopes

[23] Our lowest observations of CH_4 in air at Mount Wilson (~ 1.76 ppm) were depleted in CH_4 with respect to the nearest background air monitoring site (Figure 3a). This concentration likely represents the annual minimum in CH_4 concentration at our site, as, in general, CH_4 is lower in summer than winter in other Northern Hemisphere sites [Lowry *et al.*, 2009; Dlugokencky *et al.*, 2010]. The NOAA flask sampling network reports an average CH_4 concentration in August 2009 of 1.82 ppm at Trinidad Head, California [Dlugokencky *et al.*, 2010]. This indicates consumption of CH_4 by interaction with OH or other radicals in the urban atmosphere at our study site, which is high in concentration in the summer months [Seinfeld, 1989; Griffin *et al.*, 2004; Langford *et al.*, 2010]. Previous studies have also documented that CH_4 concentrations drop in the summer months in response to high oxidation rates in the atmosphere [Tyler *et al.*, 2007]. Our measurements of urban air at high altitude indicate that excess CH_4 in Los Angeles has a $\delta^{13}\text{C}$ of approximately -41.5‰ and a δD between -203‰ and -228‰ (Figure 4). Assuming depletion of CH_4 by 0.1 ppm that is uniform across the concentration gradient measured, we can assume that our estimates of the CH_4 end-members are depleted by up to 4‰ for $\delta^{13}\text{C}$ and 20‰ for δD [Saueressig *et al.*, 2001]. This places our end-member close to our measurements from oil fields and power plants (Figure 2). Our estimates would be improved by incorporating tracers to track air masses moving through the urban core and up to our sampling site, such as ^{222}Rn , or by incorporating measurements of other fossil fuel tracers, such as $^{14}\text{CO}_2$ or CO. Measurements of conservative tracers as well as trajectory analysis would enable us to translate our measurements into emission rates.

[24] Our data indicate that CH_4 loss from geologic formations, natural gas pipelines and/or fossil fuel refining was the major source of CH_4 in the Los Angeles Basin during our brief sampling period. Longer-term studies are needed to confirm that this is the major source of CH_4 throughout the year. This finding is in keeping with an earlier study [Wunch *et al.*, 2009], which estimated that gas leaks and other industrial sources could account for about 0.1 to 0.3 Tg CH_4 emitted in Los Angeles annually. A recent study by the California Air Resources Board also indicated that leakage from natural gas infrastructure and distribution systems ("fugitive" CH_4) may be underestimated in statewide models [Hsu *et al.*, 2010]. Estimates of fugitive CH_4 emission rates vary widely, ranging from 0.005% to 4%, [Shorter *et al.*, 1996; Kirchgessner *et al.*, 1997; Lelieveld *et al.*, 2005], with estimates for the entire natural gas industry of up to 10%, including emissions from venting and flaring [Cicerone and Oremland, 1988; Kirchgessner *et al.*, 1997]. However, there are very few published studies of fugitive CH_4 emission rates in urban areas, despite very extensive natural gas pipelines present in most cities. Studies of $\delta^{13}\text{C}-\text{CH}_4$ in Krakow, Poland, found excess CH_4 concentrations attributed to leakage from natural gas pipelines [Kuc *et al.*, 2003], and fossil fuel leakage is a significant source of

CH₄ in London, UK (~20% of total urban CH₄ emissions) [Lowry *et al.*, 2001; Fisher *et al.*, 2006]. In addition to natural gas pipelines, Los Angeles also has several large oil refineries, which process most of the crude oil from the Alaskan North Slope. These facilities are known sources of CH₄, as are electric utilities [Piccot *et al.*, 1996]. Because of the higher global warming potential of CH₄ with respect to CO₂, fugitive CH₄ emissions of even 1% of natural gas in a distribution system will increase the overall global warming potential of natural gas consumption by 25% [Howarth *et al.*, 2011]. This is a growing concern as biogas production and domestic natural gas exploration, including from shale deposits ("hydrofracking"), increases.

[25] Our measurements of $\delta^{13}\text{C}$ of CH₄ on freeways during rush hour (Table 2) do not indicate a large source of highly enriched CH₄ from vehicle emissions (Figure 2). This is not surprising, as other studies have also shown that vehicle exhaust is a minor source of atmospheric CH₄ [Tyler, 1991; Chanton *et al.*, 2000; Mays *et al.*, 2009].

[26] Direct emissions of CH₄ from vehicles are not considered a significant portion of the global CH₄ budget [Forster *et al.*, 2007]: one group estimated that direct emissions from vehicles accounted for about 0.5 Tg CH₄ yr⁻¹ globally, or about 0.2% of annual anthropogenic CH₄ emissions [Nam *et al.*, 2004]. Amendments to the Clean Air Act in 1990 restricted total hydrocarbon emissions from passenger cars to 0.16 g km⁻¹, and up to 0.24 g km⁻¹ for trucks [U.S. Environmental Protection Agency (USEPA), 2004]. Actual CH₄ emissions from gasoline-powered cars in this category (built since 1990) range from 0.007 to 0.012 g km⁻¹, with an additional 0.055 g CH₄ emitted per cold start [USEPA, 2004]. Interstate 405, the most crowded freeway in Los Angeles, has an average of 374,000 cars per day at the busiest interchanges (California Department of Transportation, Annual average daily traffic statistics, 2009, <http://traffic-counts.dot.ca.gov>). The average commuting distance in California is 40 km d⁻¹, or about 26.7 min d⁻¹ [U.S. Department of Transportation, 2001]. At 0.007 g CH₄ km⁻¹ plus an additional 0.055 g CH₄ per start (and assuming all of the cars have been built since 1990 and are started 2 times per day), vehicles contribute 227 kg CH₄ d⁻¹ in Los Angeles, or about 83,000 kg CH₄ yr⁻¹. This is only a small fraction of estimated annual CH₄ emissions in Los Angeles of between 0.2 to 0.6 Tg CH₄ yr⁻¹ (2 to 6 × 10⁸ kg yr⁻¹) [Wunch *et al.*, 2009; Hsu *et al.*, 2010].

[27] More surprisingly, our measurements do not indicate a large source of CH₄ from landfills or wastewater treatment in Los Angeles. However, in London, UK, a comparable sized city (population ~13 million), landfills are the dominant source of urban CH₄ [Lowry *et al.*, 2001; Fisher *et al.*, 2006]. Globally, landfills and wastewater are a large source of CH₄, with estimates ranging from 6 to 12% of total global CH₄ emissions [Denman *et al.*, 2007]. This contribution is expected to be much larger in urban areas, especially in generally dry regions, such as southern California, without significant wetland area. However, California regulates CH₄ emissions from landfills, and the state is at the forefront of natural gas reclamation from landfills to provide fuel for trash collection vehicles. The contribution of wastewater treatment to CH₄ emissions in Los Angeles is not well understood, and more studies are needed on the flux and stable isotopic composition of CH₄ from wastewater

treatment plants, especially as the region incorporates more biological wastewater recycling techniques to conserve freshwater resources [Townsend-Small *et al.*, 2011b]. However, our isotopic measurements do not indicate that this is a major source of CH₄ in the Los Angeles area.

4.2.2. Radiocarbon

[28] The radiocarbon content of atmospheric CH₄ is globally higher than that of CO₂, due largely to the release of radiocarbon-labeled CH₄ from nuclear power facilities and atmospheric nuclear weapons testing [Lassey *et al.*, 2007b]. Most recent evidence shows that $\Delta^{14}\text{C}$ of CH₄ of background air has increased linearly since at least the mid-1980s, to a present-day value of about 138.9 pMC (extrapolated from Figure 1 [Lassey *et al.*, 2007b]). The flux of ¹⁴CH₄ from nuclear reactors is mostly from pressurized water reactors and results from deprotonation of ¹⁴N and reaction with H₂, resulting in venting of radio-labeled CH₄ and other reduced C species [Lassey *et al.*, 2007b]. However, this flux is poorly quantified, and CH₄ from these sources is approximately 70% ¹⁴C [Lassey *et al.*, 2007a, 2007b]. At least one other study in southern California has also shown that CH₄ dissolved in surface ocean water is enriched in ¹⁴C as compared to modern C [Kessler *et al.*, 2008]. There are no nuclear power plants located directly in the Los Angeles air basin, but there is one pressurized water reactor just south of the Los Angeles basin (San Onofre Nuclear Generating Station, San Clemente; Figure 1) and one further north (Diablo Canyon Power Plant; San Luis Obispo county).

[29] Despite the radiomethane contribution from nuclear power plants, high $\Delta^{14}\text{C}$ levels in atmospheric CH₄ are tempered by the release of ¹⁴C-free CH₄ from fossil fuel sources [Wahlen *et al.*, 1989; Lassey *et al.*, 2007b]. Previous analyses of $\Delta^{14}\text{C}$ of CH₄ have found that about 20% to 30% of CH₄ globally is ¹⁴C-free, or of fossil origin [Wahlen *et al.*, 1989; Quay *et al.*, 1999; Lassey *et al.*, 2007b]. It is difficult to use our measurements of $\Delta^{14}\text{C}$ -CH₄ to calculate the fossil fuel fraction of CH₄ emissions in Los Angeles, due to high variability in our radiocarbon dates and due to the lack of relationship to CH₄ concentration. For example, our measurements of $\Delta^{14}\text{C}$ in background air (1.76 ppm) range from +261.9‰ to +339.8‰, or 127.1 to 134.9 pMC, which more or less represents the range of $\Delta^{14}\text{C}$ of CH₄ measurements along the entire concentration gradient in this study (Figure 3d and Table 3). However, our data do generally indicate the presence of fossil fuel-derived CH₄ in air in the Los Angeles basin: the current global background $\Delta^{14}\text{C}$ of CH₄ of 138.9 pMC [Lassey *et al.*, 2007b] is greater than all of the air samples analyzed in this study. Certainly more research is needed to constrain the background value of $\Delta^{14}\text{C}$ of CH₄ in air in southern California as well as other urban areas, which can aid in constraining contributions of fossil fuels to total CH₄ emissions.

4.3. Potential for Optical, in Situ Measurements to Determine Sources of CH₄ Emissions

[30] Continuous measurements of greenhouse gas concentrations, such as those presented here, will likely be essential to any attempt to monitor emissions reductions targets, and stable isotopes and radiocarbon will be extremely useful in source apportionment [Levin *et al.*, 2011]. Recent technological advances have shown that the

stable isotopic composition of CH₄ can also be measured using optical techniques, with a strong interest in constraining CH₄ sources [Quay et al., 1999; Webster and Mahaffy, 2011]. However, currently these instruments generally have decreased accuracy as compared to IRMS systems [Zare et al., 2009; Webster, 2005], and work best with CH₄ that is much higher than atmospheric concentrations and/or pressures [Bergamaschi et al., 2000; Keppler et al., 2010]. Because of the high background concentration of CH₄ in Earth's atmosphere and relatively small contribution of source CH₄, measurements of the isotopic composition of CH₄ in air with excess CH₄ are similar to those in background air. For example, in this study, $\delta^{13}\text{C}$ of CH₄ in Los Angeles air varied less than 1.5‰ along a concentration gradient from 1.7 to 2.2 ppm (Figure 3b). Until TLS instruments are able to accurately measure small (i.e., $\ll 1\%$ for $\delta^{13}\text{C}$) differences in $\delta^{13}\text{C}$ of δD of CH₄ at normal atmospheric concentrations and pressures, mass spectrometry remains the more practical tool for source determination. However, we have shown that the combination of TLS concentration measurements and IRMS isotope measurements of these parameters is a very promising tool for monitoring CH₄ emissions and source identification in urban areas or along urban-to-rural gradients. In our study, we used concentration data from the TLS instrument to time our flask sampling for later isotope analysis, so that our isotope measurements would represent the maximum possible concentration gradient.

5. Conclusions and Implications

[31] We have shown that $\delta^{13}\text{C}$ and δD of atmospheric methane can be very useful for elucidating urban sources of CH₄. We also present data on new sources of CH₄ fuel in our measurements of isotope ratios of landfill and manure bio-fuels. Radiocarbon measurements of CH₄ in our study region show that high background values of $\Delta^{14}\text{C}$ of CH₄ may be diluted by inputs of fossil fuel CH₄, but long-term monitoring is necessary to better understand the patterns of radiomethane in Los Angeles. However, stable isotope measurements of CH₄ in Los Angeles indicate that fossil fuels, not agriculture, are the dominant source of CH₄ in this region, with evidence pointing toward losses from natural gas pipelines or hydrocarbon refining as the dominant source in the region. Further work on $\delta^{13}\text{C}$ and δD of CH₄ in Los Angeles will improve our ability to quantify the strength of these CH₄ sources. This type of observation will be improved by continuous measurements of CH₄ concentration using TLS. In general, continuous measurements of greenhouse gas concentrations supplemented with isotope ratio measurements are extremely useful tools for verifying emissions reductions and for constraining regional-scale inversion modeling of emissions.

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