



# Sources of variation in $\delta^{13}\text{C}$ of fossil fuel emissions in Salt Lake City, USA

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## Abstract

The isotopic composition of fossil fuels is an important component of many studies of C sources and sinks based on atmospheric measurements of  $\text{CO}_2$ . In C budget studies, the isotopic composition of crude petroleum and  $\text{CH}_4$  are often used as a proxy for the isotopic composition of  $\text{CO}_2$  emissions from combustion. In this study, the C isotope composition ( $\delta^{13}\text{C}$ ) of exhaust from the major fossil fuel emission sources in Salt Lake City, USA, was characterized with 159 measurements of vehicle exhaust of various types and eight measurements of residential furnace exhaust. These two sources were found to be isotopically distinct, and differed from global-scale estimates based on average values for crude petroleum and  $\text{CH}_4$ . Vehicle-specific factors such as engine load and operation time had no effect on  $\delta^{13}\text{C}$  of vehicle exhaust. A small difference was found between the mean  $\delta^{13}\text{C}$  of vehicle exhaust collected randomly from different vehicles and the mean  $\delta^{13}\text{C}$  of gasoline collected from multiple fueling stations representing major gasoline distributors in Salt Lake City and the surrounding area. However, a paired comparison of  $\delta^{13}\text{C}$  of exhaust and gasoline for six different vehicles did not show any consistent C isotope fractionation during vehicle combustion. The mean  $\delta^{13}\text{C}$  of crude petroleum processed for local distribution differed slightly from refined gasoline collected at multiple fueling stations, but time lags between processing and transportation cannot be ruled out as an uncontrollable contributing factor. Measured isotope ratios were then combined with fuel consumption statistics to predict the annual cycle of  $\delta^{13}\text{C}$  of fossil fuel emissions for the Salt Lake City metropolitan area. The results showed that the isotopic composition of  $\text{CO}_2$  emissions from fossil fuel combustion varied by almost 3‰ over the course of the 2002 calendar year. This study illustrates that on a regional scale, the isotopic composition of fossil fuel emissions shows a high degree of both spatial and temporal variability that may influence characterization of C sources and sinks with atmospheric measurements.

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## 1. Introduction

The concentration of  $\text{CO}_2$  in Earth's atmosphere has increased since the time of the Industrial Revolution primarily due to the combustion of fossil fuels, which is of concern because changes in the

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concentration of CO<sub>2</sub> in Earth's atmosphere are linked to changes in climate (Petit et al., 1999; IPCC, 2001). In the current global C cycle, there are a variety of CO<sub>2</sub> sinks on both land and in the ocean that offset the atmospheric CO<sub>2</sub> increases associated with fossil fuel burning, land-use change, and biomass burning (Keeling et al., 1995; IPCC, 2001). To better understand the interactions between components of the C cycle, we need to better identify sources and sinks of CO<sub>2</sub> and quantify their relative contribution to the atmosphere at a variety of spatial scales. The isotopic composition of CO<sub>2</sub> provides a tracer that can be used to identify sources and sinks of C at local, regional, and global scales if the anthropogenic fossil fuel signals are known.

Carbon dioxide emissions from fossil fuel combustion have been estimated with energy use statistics and combined with average global values of the isotopic composition of fossil fuels to estimate the isotopic composition of emissions (Tans, 1981; Andres et al., 2000). At regional to global scales, estimates of the isotopic composition of fossil fuel emissions are needed to constrain estimates of biological and oceanic sources and sinks (Ciais et al., 1995a,b; Francey et al., 1995; Keeling et al., 1995). At the local scale, the isotopic composition of fossil fuel emissions has been used to partition CO<sub>2</sub> concentrations into their components in order to distinguish between fossil fuel CO<sub>2</sub> sources and those associated with biological activity in urban areas (Kuc and Zimnoch, 1998; Takahashi et al., 2001, 2002; Clark-Thorne and Yapp, 2003; Pataki et al., 2003; Widory and Javoy, 2003). Because the isotopic composition of fossil fuels exhibits geographical variability (Andres et al., 2000), direct measurements of local emissions are required for these studies (Pataki et al., 2005). However, there have been few, if any, intensive studies of the magnitude of temporal and spatial variability in the isotopic composition of fossil fuel emissions in a given region.

To evaluate the potential sources of variability in the C isotope composition of local fossil fuel emissions, the authors measured C isotope ratios associated with locally supplied crude petroleum and refined gasoline, as well as the C isotope ratio of fossil fuel emissions measured from vehicle and residential exhaust in Salt Lake City, UT, USA. Consideration was given to emissions from vehicles powered by different fuel types, the effects of engine load and operation time on the C isotope composition of vehicle exhaust, and emissions from residen-

tial natural gas furnaces. The goal was to evaluate and quantify sources of variability in the C isotope ratio of local CO<sub>2</sub> sources, estimate the average isotopic composition of emissions from various types of fuel combustion, and ultimately apply these data to estimating the isotopic composition of total fossil fuel emissions in the Salt Lake City metropolitan area. These data provide a means of evaluating the urban C cycle at the local scale, as well as the influence of the urban region on the global atmosphere.

## 2. Methods

### 2.1. Study site

Salt Lake City is a metropolitan area in Utah, USA, and is surrounded by the Wasatch, Oquirrh and Traverse Mountains, which reach elevations in excess of 2800 m. The city is located at elevations of 1280–1524 m above sea level and has a semi-arid climate with four distinct seasons. Mean annual temperature and precipitation are 11.1 °C and 411 mm, respectively (Alder et al., 1996). While the population of Salt Lake City proper is ca. 180,000, Salt Lake County, which covers 1979 km<sup>2</sup> surrounding the city, has a population of ca. 898,000, most of which is in the Salt Lake Valley (1275–1550 m in elevation) surrounded by mountains on three sides and the Great Salt Lake on the north (US Department of Commerce, 2001).

Approximately 85% of all residences in Utah are heated by natural gas (US Bureau of Census, 2000), such that natural gas combustion is likely to constitute a large source of CO<sub>2</sub> emissions from the region. Other large potential sources of combustion-derived CO<sub>2</sub> are combustion of gasoline and diesel fuels for transportation. There are five petroleum refineries in Utah that supply local fuel. Two of the refineries are located in Salt Lake City, and three are located within 16 km of the city. While the primary energy source for Utah is coal-fired power plants, these power plants are located in remote areas, and consequently, do not represent a source of local fossil fuel exhaust.

### 2.2. Petroleum and gasoline sample collection

According to Utah refinery receipts for the 2002 calendar year, petroleum processed for local distribution came from four geographic regions (US Department of Energy, 2002a): Wyoming, Colorado and

Utah, USA, and Alberta, Canada. Crude petroleum samples associated with the aforementioned regions were obtained from a local refinery. However, the crude petroleum associated with Wyoming and Colorado had been combined into one mixture at the refinery prior to processing due to similar physical characteristics, and consequently, the crude petroleum samples obtained were representative of three petroleum reservoirs (Wyoming and Colorado  $n = 1$ , Utah  $n = 1$ , Alberta  $n = 2$ ). Refined gasoline samples were collected from 12 gasoline stations within Salt Lake City that represented three of the five local refineries' production and one of two out of area pipeline sources (85 octane  $n = 12$ , 88 octane  $n = 12$ , 91 octane  $n = 12$ ). There was no way of knowing exact relationships between refinery samples and gasoline station samples. In addition, gasoline samples were collected for six vehicles at the time of fueling ( $n = 6$ ). These gasoline samples were collected for direct comparison with tailpipe exhaust obtained from each vehicle.

### 2.3. Exhaust sample collection

To determine the appropriate method for collecting exhaust samples, four methods were tested for isotope fractionation by collecting exhaust samples from the tailpipe of the same vehicle over an approximate 2 h time period. All exhaust samples were collected in 100 mL glass flasks (model 34-5671, Kontes, Vineland, NJ, USA) as follows: evacuated flasks were attached to a toggle switch ( $n = 4$ ), evacuated flasks were attached to a 1- $\mu\text{m}$  Gelman filter ( $n = 6$ ), flasks were flushed with exhaust air using a pump attached to a  $\text{Mg}(\text{ClO}_4)_2$  water trap ( $n = 7$ ), and evacuated flasks were used without any attachment ( $n = 6$ ). In each case, the elements of the sampling apparatus were connected to each other and to the tailpipe via Dekoron<sup>®</sup> tubing (Fig. 1). In order to ensure that the air collected in the glass flasks was only exhaust, the tubing at the tailpipe end of the sampling apparatus was held just inside the tailpipe.

The results of this test showed that there was no significant difference in the C isotope composition of exhaust based on the various collection methods tested (ANOVA,  $p > 0.05$ , Fig. 2). Thus, the authors chose to collect exhaust samples using evacuated flasks attached to a filter in order to facilitate collection of a large number of exhaust samples in a short period of time.

Exhaust gases were collected from a total of 80 gasoline-powered vehicles. Due to seasonal differ-

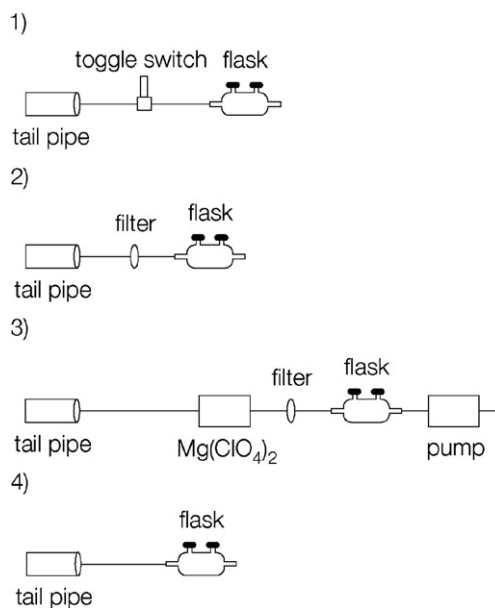


Fig. 1. Schematic showing the various methods used to collect vehicle exhaust in order to determine the appropriate exhaust sampling method.

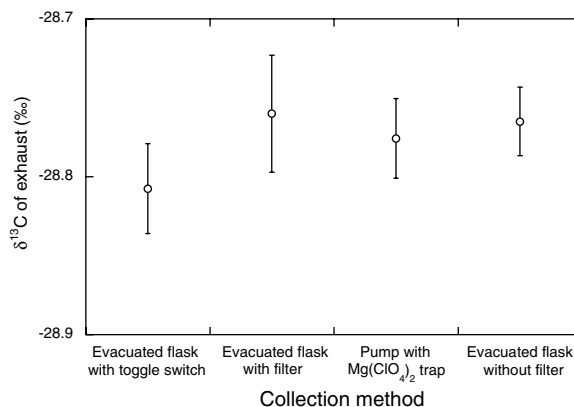


Fig. 2. The isotopic composition of vehicle exhaust collected from a single vehicle, using various collection methods over the course of an approximate 2 h time period. Error bars represent  $\pm 1$  standard error.

ences in the composition of gasoline, vehicle exhaust was collected during both the summer and winter seasons. In order to randomize sample collection, winter season samples were collected from vehicles accessing a commercial drive-through window and summer season samples were collected at a major intersection during periods when vehicles were stopped due to traffic signaling. Exhaust from two additional vehicles was collected as a time series, in which samples were collected initially after starting

the engines, and again at 10 min intervals until 10 samples for each vehicle had been collected. The time series represented exhaust collected over a period of 100 min of continuous engine use. Eighteen exhaust samples were also collected from six vehicles for direct comparison with the gasoline combusted for each vehicle.

Diesel exhaust was collected from 79 diesel buses associated with the Utah Transit Authority bus fleet. Additionally, 40 samples of diesel exhaust were collected from a diesel engine located at the University of Utah combustion research facility. The diesel engine was a two-cylinder Kubota model Z482B with 482 cc displacement. The engine was equipped with torque load control, absorbed load through the entire torque range, and was equipped with automated computer data acquisition. The exhaust samples obtained from this engine represent a range of different engine load conditions.

Natural gas exhaust samples were collected from eight residential furnaces located throughout different parts of Salt Lake City.

#### 2.4. Isotope analysis

Isotope ratios are expressed in  $\delta$  notation as the C isotope ratio relative to the ratio of a known standard (V-PDB):

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\text{‰} \quad (1)$$

where  $R$  is the ratio of heavy to light isotopes of the sample and standard.

Samples of crude petroleum and gasoline with varying octane content were prepared for C isotope ratio analysis via offline combustion using quartz tubing (Boutton et al., 1983). The resulting  $\text{CO}_2$  was isolated inside sealed glass tubing using a vacuum line and cryogen traps, and measured with an isotope ratio mass spectrometer (Finnigan MAT Delta S; Bremen, Germany) by dual inlet; the overall precision of these measurements was  $\pm 0.16\text{‰}$ . The isotopic composition of  $\text{CO}_2$  in exhaust was measured with an isotope ratio mass spectrometer (Finnigan MAT Delta S; Bremen, Germany) operating in continuous flow mode; the overall precision of these measurements was  $\pm 0.15\text{‰}$ .

#### 2.5. Statistical analysis

Statistical analyses were performed using InStat 3 (<http://www.graphpad.com>) and Kaleidagraph (<http://www.synergy.com>) software. Statistical tests

included one-way and two-way analysis of variance (ANOVA) tests, Bonferroni multiple comparisons test, Kruskal–Wallis test (non-parametric ANOVA), unpaired  $t$ -test, paired  $t$ -test, and simple linear regression.

### 3. Results

Crude petroleum obtained from the local refinery had C isotope ratios (ANOVA,  $p < 0.05$ ) ranging from  $-25.9\text{‰}$  to  $-31.5\text{‰}$ , which was within the reported literature range for crude petroleum in associated geographic regions (Table 1).  $\delta^{13}\text{C}$  of refined gasoline samples obtained from various distributors were all significantly different (ANOVA,  $p < 0.05$ ), with the range of mean values between  $-26.7\text{‰}$  and  $-28.8\text{‰}$  (Table 2). The octane content of gasoline did not significantly influence the C isotope ratio (two-way ANOVA,  $p > 0.05$ ). All samples of refined gasoline combined had a mean value of  $-27.7 \pm 0.15\text{‰}$ . In contrast, mean  $\delta^{13}\text{C}$  of vehicle exhaust measured in the same season was  $-28.4 \pm 0.10\text{‰}$ . The comparison of paired gasoline and exhaust samples obtained for six vehicles indicated a significant positive correlation (linear regression,  $p < 0.05$ , Fig. 3). Because the regression intercept was not significant ( $p > 0.05$ ), the regression was forced through the origin. The resulting best-fit slope was  $1.01 \pm 0.01$  (Fig. 3). When data for all six vehicles were combined, the mean value for refined gasoline was  $-28.1 \pm 0.28\text{‰}$  and was not significantly different from the mean for exhaust, which was  $-28.4 \pm 0.31\text{‰}$  (paired  $t$ -test,  $p > 0.05$ ).

Samples collected during an extended period of vehicle idling showed that engine operation time had no significant effect on the C isotope ratio of exhaust  $\text{CO}_2$  (linear regression,  $p > 0.05$ , Fig. 4). Additionally, varying engine loads applied to a diesel engine had no effect on the C isotope ratio of exhaust  $\text{CO}_2$  (linear regression,  $p > 0.05$ , Fig. 5).

The  $\delta^{13}\text{C}$  of exhaust  $\text{CO}_2$  collected from vehicle combustion of summer gasoline and diesel fuel were not significantly different (Kruskal–Wallis test,  $p > 0.05$ ); the overall mean  $\delta^{13}\text{C}$  of  $\text{CO}_2$  for exhaust from diesel and summer fuel was  $-28.5 \pm 0.04\text{‰}$ . In contrast, winter gasoline was slightly enriched at  $-27.9 \pm 0.08\text{‰}$  (Kruskal–Wallis test,  $p < 0.05$ ). The C isotope ratio of natural gas combustion was  $-37.1 \pm 0.20\text{‰}$  and was significantly different from that of gasoline or diesel (Kruskal–Wallis test,  $p < 0.05$ , Fig. 6).

Table 1

The C isotope composition ( $\delta^{13}\text{C}$ , V-PDB) of crude oil (mean  $\pm$  the standard error where applicable)

Crude petroleum area source	Measured in Salt Lake City, USA		Reported literature range <sup>a</sup>	
	$\delta^{13}\text{C}$ (‰)	<i>n</i>	$\delta^{13}\text{C}$ (‰)	<i>n</i>
Alberta, Canada	$-29.1 \pm 0.03$	2	-27.6 to -31.1	7
Uinta Basin, UT, USA	-31.5	1	-27.8 to -31.7	14
Wyoming and Colorado, USA	-25.9	1	-25.7 to -29.6	29

Crude oil samples processed at a local petroleum refinery are compared with literature values for geographic locations relevant to Utah crude oil imports. Refinery samples represent an integrated value for the source locations listed, as the crude oil from the above listed regions are combined based on similar physical characteristics prior to processing. The sample size (*n*) refers to the number of crude oil samples.

<sup>a</sup> Carbon isotope values of petroleum were obtained from Yeh and Epstein (1981), Chung et al. (1981) and Silverman and Epstein (1958).

Table 2

The C isotope composition ( $\delta^{13}\text{C}$ , V-PDB) of gasoline in Salt Lake City, Utah (mean  $\pm$  the standard error)

Gasoline distributors	$\delta^{13}\text{C}$ (‰)	<i>n</i>
Sinclair	$-28.8 \pm 0.07^a$	9
Chevron	$-28.2 \pm 0.05^b$	9
Tesoro	$-27.3 \pm 0.06^c$	9
Phillips 66	$-26.7 \pm 0.26^d$	9

Chevron, Tesoro, and Phillips 66 distributors were supplied by separate local refineries, while the Sinclair distributor was supplied primarily by an out of area pipeline. The sample size (*n*) refers to the number of gasoline samples analyzed for each distributor. The gasoline samples were collected from three independent fueling stations for each distributor type. Upper scripts a–d denote statistically significant mean differences (ANOVA,  $p < 0.05$ ).

The mean  $\delta^{13}\text{C}$  of  $\text{CO}_2$  for gasoline, diesel, and natural gas exhaust were applied to Utah fuel use statistics to obtain monthly estimates of the isotopic composition of total fossil fuel emissions, assuming that the major sources are vehicle emissions and natural gas combustion, and applying fuel-specific emissions factors (US Environmental Protection Agency, 1998; US Department of Energy, 2002b,c). To estimate the emissions for Salt Lake County, population and employment ratios were applied as described by the Utah Department of Environmental Quality (1996). Emission calculations were made on a monthly basis for the 2002 calendar year to correspond with the period that exhaust samples were collected. Average values

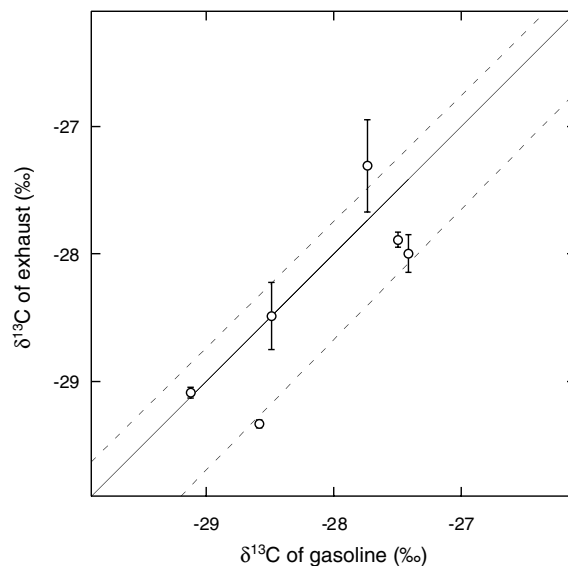


Fig. 3. Correlation of the isotopic composition of paired gasoline and exhaust samples for six vehicles. The solid line (—) represents the best-fit slope of 1 and was forced through the origin, as the intercept was not significant ( $p > 0.05$ ). The dashed lines (---) represent 95% confidence intervals. Error bars represent  $\pm 1$  standard error.

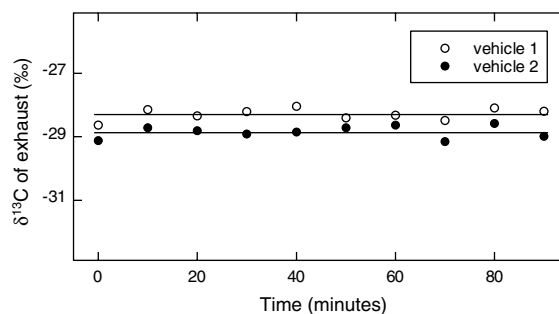


Fig. 4. The isotopic composition of vehicle exhaust collected from two vehicles during 100 min of continuous engine use. The solid lines represent the average C isotope ratio ( $\delta^{13}\text{C}$ ) for each vehicle. The lines show a slope of zero, as there was no significant change in  $\delta^{13}\text{C}$  with time ( $p > 0.05$ ).

associated with the isotopic composition of major exhaust sources were applied to total  $\text{CO}_2$  emissions as:

$$\delta^{13}\text{C}_T = \delta^{13}\text{C}_N(F_N) + \delta^{13}\text{C}_G(1 - F_N) \quad (2)$$

where  $\delta^{13}\text{C}_T$  is the C isotope composition of total emissions from natural gas and gasoline combustion,  $\delta^{13}\text{C}_N$  is the average C isotope composition of natural gas exhaust from residential furnaces,  $F_N$  is the fraction of total emissions associated with natural gas combustion, and  $\delta^{13}\text{C}_G$  is the average C isotope composition of vehicle exhaust.

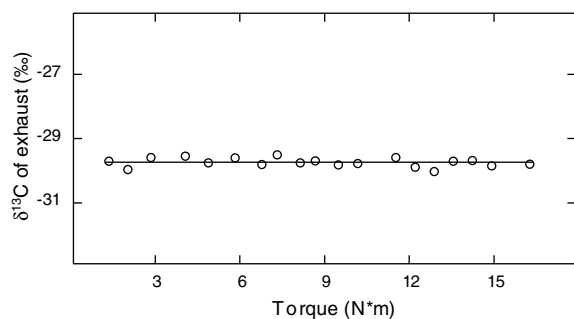


Fig. 5. The C isotope composition ( $\delta^{13}\text{C}$ ) of exhaust under varying engine loads. The solid line shows a slope of zero, as there was no significant change in  $\delta^{13}\text{C}$  with engine load ( $p > 0.05$ ).

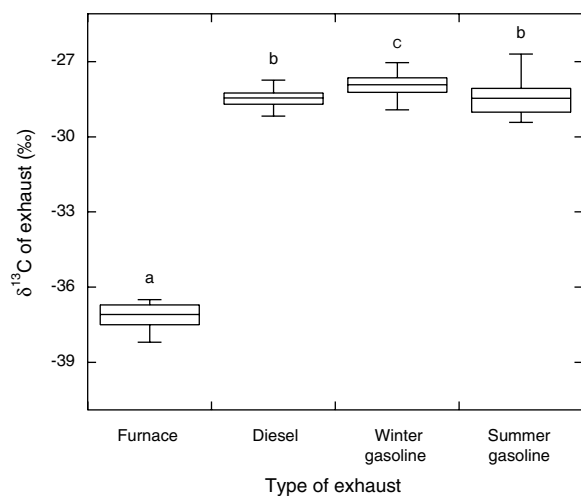


Fig. 6. The isotopic composition of exhaust collected from the major fossil fuel emission sources in Salt Lake City, USA. The boxes show the inter-quartile range and median values of each exhaust type while the bars show the maximum and minimum. Letters indicate statistical differences (non-parametric ANOVA Kruskal–Wallis test,  $p < 0.05$ ).

The results of these calculations showed a large seasonal cycle that ranged from  $-30.8\text{‰}$  in mid-summer to  $-33.5\text{‰}$  in winter (Fig. 7).

## 4. Discussion

### 4.1. Predicting $\delta^{13}\text{C}$ of fossil fuel emissions

In this study, the  $\delta^{13}\text{C}$  of crude petroleum was variable, but not as variable as known global variations. Globally,  $\delta^{13}\text{C}$  of crude petroleum varies from  $-19\text{‰}$  to  $-35\text{‰}$ , depending on geographic origin (Tans, 1981; Andres et al., 2000). It was found that for the Salt Lake County region,  $\delta^{13}\text{C}$  of crude petroleum showed a fairly high degree of variability,

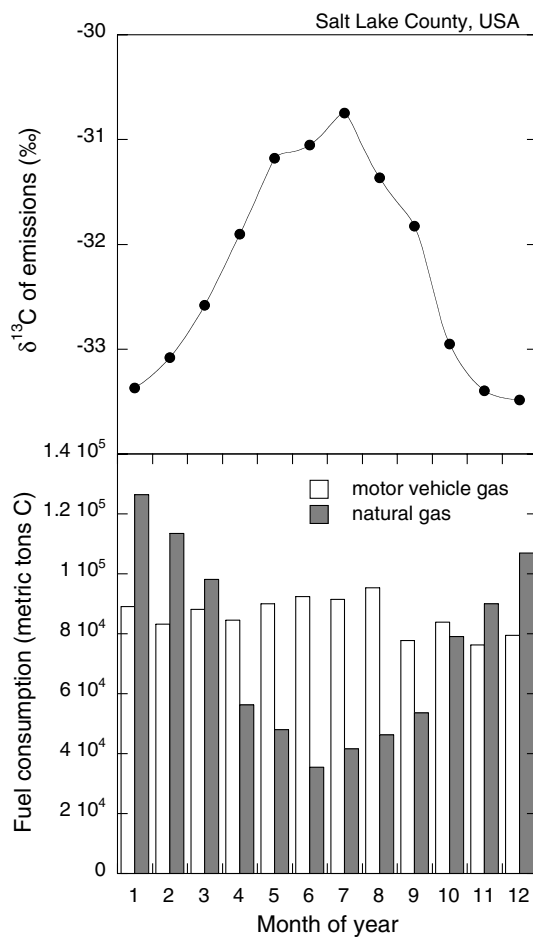


Fig. 7. The annual course of  $\delta^{13}\text{C}$  of fossil fuel emissions from motor vehicle gas and natural gas combustion in Salt Lake County, USA (upper panel) obtained by combining fuel consumption statistics (lower panel) with the average isotopic composition of vehicle and furnace exhaust.

with samples from a single refinery ranging from  $-25.9\text{‰}$  to  $-31.5\text{‰}$  with a mean of  $-28.8 \pm 1.6\text{‰}$  (Table 1). These values were consistent with previously reported data from the same geographic regions (Silverman and Epstein, 1958; Chung et al., 1981; Yeh and Epstein, 1981), although the mean value for crude petroleum differed from the global weighted mean value by  $2.3\text{‰}$ .

The variation in  $\delta^{13}\text{C}$  of refined gasoline was smaller than that observed for crude petroleum, and mean values of  $\delta^{13}\text{C}$  associated with refined gasoline and crude petroleum were different.  $\delta^{13}\text{C}$  of refined gasoline including samples from all distributors ranged from  $-26.2\text{‰}$  to  $-29.2\text{‰}$ . The mean  $\delta^{13}\text{C}$  of  $-27.7 \pm 0.15\text{‰}$  associated with refined gasoline samples was slightly enriched relative to the

average of measured crude petroleum values. An exact correspondence between the average crude petroleum and refined gasoline values was not necessarily expected, as there is the potential for fractionation during the refining process, and the averages were not weighted based on the actual amounts of crude petroleum from each source region used to produce the gasoline associated with the samples. Based on refinery reports, the amount of crude petroleum from each source region that was refined during the study period did vary (US Department of Energy, 2002a), although quantifying the amount and distribution of each petroleum source associated with the gasoline samples collected was not possible. However, the results suggest that estimates of  $\delta^{13}\text{C}$  of crude petroleum versus refined gasoline are not interchangeable, and the selection of one particular set of values for estimating the isotopic composition of gasoline-derived  $\text{CO}_2$  emissions can influence  $\text{CO}_2$  partitioning results and lead to errors in regional  $\text{CO}_2$  accounting. In this study, these estimates varied by 1.1‰. While all comparisons of  $\delta^{13}\text{C}$  of refined gasoline from different fuel distributors yielded small, yet significant differences (Table 2), no difference was observed in  $\delta^{13}\text{C}$  of fuels of varying octane content. The maximum mean difference of 2.1‰ observed among distributors for refined gasoline was smaller than the maximum difference of 5.6‰ observed for crude petroleum samples. In general, blending of crude petroleum sources during the production and distribution process appeared to result in more uniform  $\delta^{13}\text{C}$  values of local refined gasoline samples than in the original petroleum sources. The mean refined gasoline estimate was 1.2‰ more depleted than the global estimate of  $\delta^{13}\text{C}$  of gasoline-derived fossil fuel emissions based on weighted mean values of crude petroleum (Tans, 1981; Andres et al., 2000).

#### 4.2. The isotopic composition of $\text{CO}_2$ in vehicle exhaust

$\delta^{13}\text{C}$  of  $\text{CO}_2$  derived from gasoline combustion was not affected by engine operation time (Fig. 4) and engine load (Fig. 5). Therefore these factors were neglected in assessing the C isotope composition of vehicle exhaust. However,  $\delta^{13}\text{C}$  of gasoline collected before combustion was comparable overall with vehicle exhaust collected from the same vehicle, as the relationship between gasoline and exhaust  $\delta^{13}\text{C}$  did not have an intercept ( $p > 0.05$ ) and the

slope had a value of 1 ( $1.01 \pm 0.01$ , Fig. 3). Although there was some scatter in the relationship, there does not appear to be a consistent fractionation of C isotopes in combustion.

As expected,  $\delta^{13}\text{C}$  of  $\text{CO}_2$  was distinct between vehicle and residential natural gas furnace exhaust (Fig. 6). However, the absolute values differed somewhat from measurements at other locations. Clark-Thorne and Yapp (2003) observed an average  $\delta^{13}\text{C}$  of  $-27.2\text{‰}$  for vehicle emissions in Dallas, TX, USA, while Widory and Javoy (2003) observed an average  $\delta^{13}\text{C}$  of  $-28.8\text{‰}$  in Paris, France. For natural gas, Clark-Thorne and Yapp (2003) reported an observation of  $-42\text{‰}$  representing laboratory natural gas combustion-derived  $\text{CO}_2$  in Dallas. Widory and Javoy (2003) reported an average value of  $-39.1\text{‰}$  for natural gas exhaust from a variety of heating sources in Paris. In general,  $\delta^{13}\text{C}$  of natural gas exhibits considerable natural variation. The main constituent of natural gas is  $\text{CH}_4$ , which shows variation in  $\delta^{13}\text{C}$  from  $-20\text{‰}$  to  $-100\text{‰}$  (Andres et al., 2000). In the current study,  $\delta^{13}\text{C}$  of  $\text{CO}_2$  derived from natural gas combustion was  $-37.1 \pm 0.20\text{‰}$ , and differed from previous global scale natural gas emission estimates of  $-44.0\text{‰}$  and  $-41.0\text{‰}$  by 6.9‰ and 3.9‰, respectively (Tans, 1981; Andres et al., 2000).  $\delta^{13}\text{C}$  of vehicle exhaust  $\text{CO}_2$  from all vehicle sources in the current study was  $-28.3 \pm 0.04\text{‰}$ , 1.8‰ more depleted than the global scale estimate of  $-26.5\text{‰}$  based on the modal value of  $\delta^{13}\text{C}$  of crude petroleum (Tans, 1981; Andres et al., 2000).

#### 4.3. The annual course of $\delta^{13}\text{C}$ of fossil fuel emissions

Direct measurements of the isotopic composition of major exhaust sources were used to predict the isotopic composition of total fossil fuel emissions in Salt Lake County, USA. Because Salt Lake County has four distinct seasons, it was expected that the C isotope ratio of total fossil fuel emissions would change over the course of the year as the consumption of natural gas for residential heating increased dramatically during winter. It was found that the calculated C isotope ratio of fossil fuel emissions for Salt Lake County varied by almost 3‰ over the course of the 2002 calendar year, with the most  $^{13}\text{C}$  depleted values in the winter and  $^{13}\text{C}$  enriched values in the summer (Fig. 7). Temporal variability in the isotopic composition of  $\text{CO}_2$  emissions is an important factor in local to regional scale studies of C sources and sinks that utilize atmospheric

observations of the isotopic composition of CO<sub>2</sub>. Assumption of a single or constant value for the fossil fuel signature could introduce significant error on short time scales.

Seasonal changes in the isotopic composition of fossil fuel emissions at local and regional scales have been previously reported from measurements of the isotopic composition of atmospheric CO<sub>2</sub> (Meijer et al., 1996; Kuc and Zimnoch, 1998; Pataki et al., 2003). However, efforts to pair these measurements with fuel consumption statistics and their assumed isotopic composition have often not yielded similar results (Meijer et al., 1996; Kuc and Zimnoch, 1998). It is possible that improved characterization of the isotopic composition of major sources of fossil fuel emissions would be helpful in reducing discrepancies in the results of bottom-up emissions inventories and top-down integrated atmospheric calculations.

## 5. Conclusions

The results showed that mean  $\delta^{13}\text{C}$  of exhaust from randomly collected samples yielded different results compared to those obtained for the isotopic composition of crude petroleum and refined gasoline associated with the study area, leading to the possibility of over- or under-estimating C sinks as a result of biases in the estimates of the isotopic composition of fossil fuel sources. The authors conclude that estimates of  $\delta^{13}\text{C}$  of fossil fuel emissions for local C balance studies should be obtained with direct local measurements of exhaust, as there is considerable geographic variability in estimates of  $\delta^{13}\text{C}$  of emissions based on both  $\delta^{13}\text{C}$  of fossil fuels and  $\delta^{13}\text{C}$  of direct exhaust measurements. The evaluation of methodology showed that a large number of samples can be obtained rapidly with the use of evacuated flasks without the need for pumps or desiccating traps if the purpose of the measurement is evaluation of  $\delta^{13}\text{C}$  in CO<sub>2</sub> (Fig. 2). Given that the C isotope composition of fossil fuel emissions is often an important component in calculations of CO<sub>2</sub> fluxes, incorporating regional and seasonal patterns in  $\delta^{13}\text{C}$  of fossil fuel emissions into model calculations should be useful in gaining a better understanding of the temporal and spatial heterogeneity in C sources and sinks at a variety of scales.

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