

Isotopic composition of CO₂ in gasoline, diesel and natural gas combustion exhaust in Vancouver, BC, Canada

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Abstract

The isotopic composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in atmospheric carbon dioxide (CO₂) originating from gasoline and diesel vehicle exhaust and from natural gas combustion was determined. Gasoline and diesel samples were taken in the exhaust of representative vehicles of the fleet in Vancouver, BC, Canada between November 2013 and May 2014. The fleet average gasoline exhaust (which contained a fraction bioethanol) was determined with a $\delta^{13}\text{C}$ of $-27.27 (\pm 0.93) \text{‰}$ and a $\delta^{18}\text{O}$ of $-12.46 (\pm 3.45) \text{‰}$ (w.r.t. VPDB-CO₂). The fleet average for diesel vehicles exhibited a slightly lower $\delta^{13}\text{C}$ of $-28.81 (\pm 0.40) \text{‰}$ and a $\delta^{18}\text{O}$ of $-18.63 (\pm 0.72) \text{‰}$ close to unfractionated combustion. For natural gas, samples were taken from an open torch using the city's natural gas supply network at different dates over the year. The mean $\delta^{13}\text{C}$ for natural gas samples was $-41.64 (\pm 0.82) \text{‰}$, while the mean $\delta^{18}\text{O}$ was lower than for internal combustion engines at $-22.74 (\pm 0.56) \text{‰}$. In conclusion, $\delta^{13}\text{C}$ depends on the fuel type and origin and there is evidence that $\delta^{18}\text{O}$ is fractionated in the combustion process and presence and state of catalytic converters causes different $\delta^{18}\text{O}$.

Introduction

The urban atmosphere contains carbon dioxide (CO₂) usually above the global background. Urban air is enriched by CO₂ originating from fuel emissions (vehicle exhaust, heating systems, gas stoves) and human, soil and plant respiration (possibly modulated by photosynthesis). For urban-scale emission monitoring it is essential to separate those sources (Christen, 2014). Due to the range of varying sources, determining the relative contribution to the observed total concentrations of CO₂ in an urban atmosphere is challenging. Utilizing the isotopic signatures of CO₂ can add valuable information. For example, the geological processes involved in the formation of different types of fossil fuels influence the relative ratio of the abundant ^{12}C to the heavier ^{13}C (the normalized ratio of the two is expressed as $\delta^{13}\text{C}$ in CO₂). By analyzing the $\delta^{13}\text{C}$ in CO₂, previous work has been able to distinguish between CO₂ emitted via gasoline combustion (less depleted in $\delta^{13}\text{C}$) vs. or natural gas combustion (more depleted in $\delta^{13}\text{C}$) (e.g. Pataki et al., 2003). Likewise, the abundant ^{16}O in CO₂ may be substituted with ^{18}O , giving $^{12}\text{C}^{18}\text{O}^{16}\text{O}$. The difference between $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}_2$ is expressed as $\delta^{18}\text{O}$ in CO₂. During combustion, the oxygen originates from the atmosphere. $\delta^{18}\text{O}$ of atmospheric oxygen is usually assumed to be constant. Hence differences in $\delta^{18}\text{O}$ are not caused by differences of the fuel or background, but differences in the combustion process and the consequent catalytic conversion (if applicable) and could be used as another indicator of sources.

Fuel for vehicles, like gasoline, can originate from a number of different commercial suppliers which sell fuel from differing geographic origins. Consequently, the isotopic signatures of fuels have been shown to vary over time, mostly due to changes in fuel imports from different geographic locations (Bush et al., 2007). Each urban region and time might therefore have slightly different values in $\delta^{13}\text{C}$.

The aim of this study is to determine the extent to which fuels from varying sources influence the isotopic composition of the CO₂ emitted in Vancouver, BC, Canada over the course of 8 months.

Quantifying the typical isotopic signature of CO₂ emitted from different sources will generate valuable data for and emission source attribution efforts or multiple source mixing models (e.g. Djuricin et al., 2010) specifically for the Metro Vancouver region.

Methods

Exhaust samples were taken and analyzed from a number of different vehicles including motorbikes, small cars, trucks, and buses, as well as natural gas. Using a laser spectrometer, it was possible to analyze the composition of the CO₂ and acquire the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in CO₂ for each sample in several repeating samples.

Field sampling

Vehicle Exhaust Sampling

Setup: Exhaust samples were taken using a rubber-coated metal tube connected to a plastic tube, which was connected to a 10 litre 'lung sampler' (Scentroid Vacuum Chamber, IDES Canada Inc., Markham, ON, Canada). The purpose of the metal tube was to avoid melting any part of the sampling apparatus while sampling the hot exhaust in the exhaust pipe (Figure 1). Inside the lung sampler is a 3 l TEDLAR bag. A Pall Corporation Acro 50 filter (1.0 μm PTFE) is located between tube and the TEDLAR bag to filter aerosols and black carbon.

Procedure: Once sampling is ready to begin (vehicle in idling mode), the metal tube is placed in the exhaust pipe of the vehicle. The end of the tube is placed approximately 10 cm into the exhaust pipe to ensure high CO₂ concentrations and that the elevated CO₂ is originating from the exhaust and not from the operator or any other sources. Immediately before turning the lung sampler on, a syringe is used to flush the tube and filter and replace any air already present in the tube with exhaust air while running the engine. Then a TEDLAR bag is attached and the vacuum chamber is closed and turned on. Sampling takes approximately one minute per bag, and the bags are filled to about 80-90 percent capacity. The exact time the bag sampling begins and ends is recorded, along with information on the vehicle's age, model, fuel type, and location (gas station) of last fuel-up, if available. From each vehicle at least two and up to four bags are sampled. Between sampling different vehicles, the tubes are flushed with ambient air using a syringe to purge from them any residual exhaust. In addition, one or two bag samples of ambient air from the sampling site are taken each time to account for background air values (unless measurements were done on the campus of the University of British Columbia (UBC), where background atmospheric air was continuously measured).

Many different vehicles were sampled, including small cars, semi trucks, buses, and motorbikes, all with varying fuel types. A total of 31 cars and trucks, 4 buses and 1 motorbike were sampled in this study from November 2013 to May 2014. Only samples exceeding 10'000 ppm CO₂ are considered in the subsequent analysis.

Natural Gas Sampling

Setup: The natural gas samples are all taken indoors in an unoccupied laboratory on UBC campus (MCML building Rm 102A). There is one natural gas supplier in Vancouver that also supplies to UBC. With the vacuum chamber and bag ready, a Bunsen burner hooked up to a natural gas source on campus is lit and run. A 3000 ml Pyrex beaker is placed upside down over the flame, so that the top of the burner is the same level as the edge of the beaker. To support the beaker, a metal ring stand is placed over the burner (see Figure 2). The metal tube attached to the vacuum chamber is placed up, and into the downturned beaker that accumulates the exhaust by about 2 cm. The tube is not placed too far into the beaker as the apparatus gets extremely hot.

Procedure: Similar to the vehicle exhaust samples, the tube is flushed with ambient room air using a syringe before sampling, and ambient room air samples are taken before and after any measurements. Once the vacuum chamber is switched on and a sample is being drawn, anyone present leaves the room to reduce excessive exhaled CO₂ affecting measurements. Only samples exceeding 10'000 ppm CO₂ are considered in the subsequent analysis.

A total of 15 samples collected between February 2014 and May 2014 were considered in the subsequent analysis. Sampling was spaced a few weeks apart to account for any possible shift in geographic gas origin.



Figure 1 – Taking exhaust measurements from a metal tube inserted into the idling car's exhaust pipe using the lung-sampler (black box).

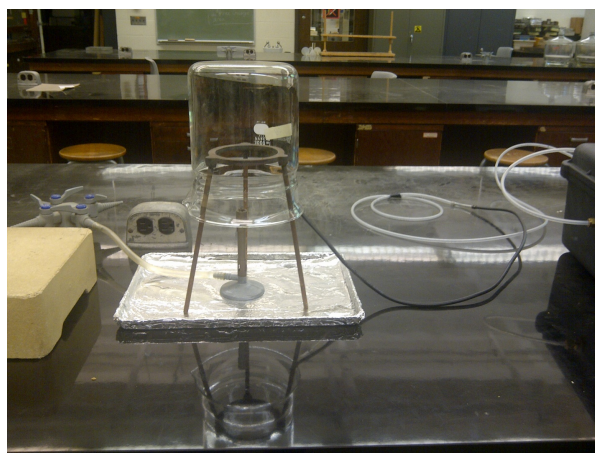


Figure 2 – The setup for sampling natural gas. A Bunsen burner is placed under a downturned beaker which is resting on a ring stand. The lung sampler (to the right) draws a sample of gas via the metal tube placed just inside the beaker.

Lab analysis

Once samples were collected they were analyzed using a tuneable laser spectrometer (TGA200, Campbell Scientific Inc., Logan UT, USA). However, before a detailed analysis can be done, samples need to be diluted. With the TGA in uncalibrated mode samples were drawn from the undiluted bag samples, and an a priori estimate of the CO₂ mixing ratios was performed on each bag to calculate the required amount to reach a CO₂ mixing ratio between 380 and 480 ppm. The reason to be between 380 and 480

ppm is because the laser spectrometer's response is calibrated to this range, using two bracket gases of roughly 380 and 480 ppm. A clean 3 litre TEDLAR bag is filled with Ultra Zero Air for every sample (bag of undiluted exhaust, ambient air, and/or natural gas). Using a syringe, the appropriate amount of undiluted sample is carefully added to the bag of Ultra Zero Air (Praxair). The syringe is always properly cleaned with Ultra Zero Air between bags, and is attached before the bag's nozzle is opened to avoid leakage or contamination.

Once the bags of diluted samples have been assembled, the diluted samples are analyzed by the TGA. The TGA automatically switches between sampling the diluted bag, and 3 other sources; It switches between sampling a "low" calibration tank, a "high" calibration tank, a flush of ambient air in the range of the sample (collected via the vacuum chamber), and the diluted sample being analyzed. Each sample is run through the TGA twice, and during each analysis the TGA must run through one full cycle. The cycle is as follows: Low Tank – Flush – Sample – Flush – High Tank – Flush – Sample – Flush – Low Tank. 'Flush' refers to three seconds of sampling of a bag of ambient concentration to avoid pressure differences. Table 2 shows the concentrations used over time for the "low" and "high" calibration gases during this study. All results in this report are shown against the VPDB-CO₂ standard (Coplen, 1995).

Table1: Mixing ratios, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ for CO₂ in each calibration tank used as either low brackets or high brackets w.r.t. VPD-CO₂. The secondary calibration tanks below have been calibrated in several iterations each relative to global National Oceanic and Atmospheric Administration (NOAA) standards at 390 and 460 ppm. Those primary standards were analyzed for isotopes at the Stable Isotope Lab (SIL) at INSTAAR, University of Colorado, in cooperation with the Global Monitoring Division of NOAA.

Calibration tank ID	Total CO ₂ (ppm)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Start Date/Time – End Date/Time (UTC) of use of tank
(Low bracket) CO2-007	399.095	-33.424	-8.636	2013/10/25 (00:00) – 2014/01/14 (20:10)
(Low bracket) CO2-009	369.880	-33.471	-8.779	2014/01/14 (20:10) – 2014/05/02 (23:00)
(Low bracket) CO2-012	380.027	-40.691	-23.634	2014/05/02 (23:00) – 2014/05/26 (00:06)
(High bracket) CO2-008	457.820	-37.165	-15.318	2013/10/25 (00:00) – 2014/01/14 (20:10)
(High bracket) CO2-011	456.872	-37.135	-15.463	2014/01/14 (20:10) – 2014/05/26 (00:06)

Once the mixing ratios of the diluted samples of CO₂ in ppm, $\delta^{13}\text{C}$ ‰, and $\delta^{18}\text{O}$ ‰ have been determined, results are either accepted or rejected based on how closely the 2 samples match. For an analysis to be verified, the difference in the acquired CO₂ concentrations and isotope ratios between the first and second blocks need to be below thresholds set by the instrument's noise. Figure 3 shows how this can be determined graphically; an analysis is verified if after the 150th sample (15 seconds) the red and blue lines have converged, as well as the pink and orange lines. For acceptable samples, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, as well as the total mixing ratios of the samples are averaged between the two runs compiled into a spreadsheet for further analysis.

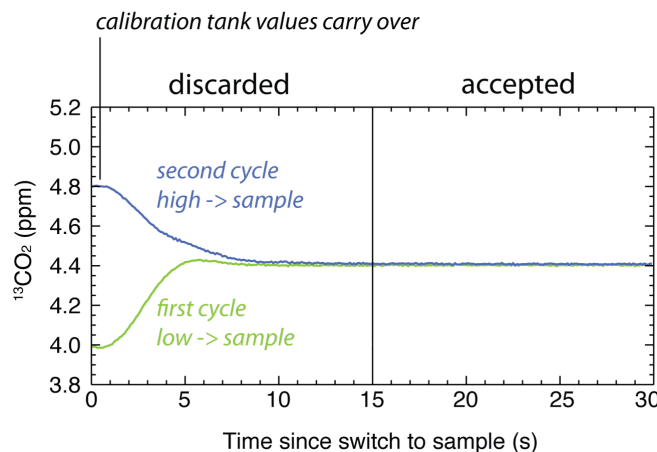


Figure 3: Measurements taken by the TGA at 10 Hz resolution while a sample bag is connected. The green and blue lines are the two cycles from the low tank and the high tank to the sample. The sample volume of the TGA needs to be flushed (contains calibration gas at time 0 seconds) and replaced by the bag content. The two cycles are converging at around the 100th reading (10 seconds), and remaining stable thereafter. Only data after the 150th reading (15 seconds) is considered and used in the analysis.

Corrections

Measurements are then corrected for ‘contamination’ by background CO₂ as follows:

$$\delta^{13}\text{C} = s \delta^{13}\text{C}_{\text{samp}} \frac{1}{[^{12}\text{CO}_2]}$$

where $\delta^{13}\text{C}$ is the corrected final isotope ratio of sample. $\delta^{13}\text{C}_{\text{samp}}$ is the measured isotope ratio of the sample (measured by the TGA contains a small fraction of background air CO₂), and $[^{12}\text{CO}_2]$ is the undiluted mixing ratio of the sample. The slope s of the Keeling plot is calculated based on the simultaneously taken background air sample (undiluted):

$$s = \frac{\delta^{13}\text{C}_{\text{back}} - \delta^{13}\text{C}_{\text{samp}}}{\left(\frac{1}{[^{12}\text{CO}_2]_{\text{back}}} - \frac{1}{[^{12}\text{CO}_2]_{\text{samp}}}\right)}$$

$\delta^{13}\text{C}_{\text{back}}$ is the measured isotope ratio of CO₂ in the background air at the sampling site (for natural gas this is indoor air). Because all exhaust samples had high mixing ratios (>10,000 ppm or 1 %, usually rather 10%), the correction was usually not very substantial, yet was applied.

3. Results and Discussion

The three fuel types (gasoline, diesel and natural gas) are reported separately. The mean and standard deviation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were calculated for all samples and compiled into 3 tables based on fuel type below (Tables 2, 3, and 4). Because there are replicates of most samples (all samples have at least two replicates, but some are not included as they failed the analysis), the average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the

replicates for each vehicle is calculated and shown on each line of tables 2, 3 or 4. For example, CAR023 was analyzed four times, yielding four replicates. The average of the four replicates is taken to reduce uncertainty. In order to derive the average $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for all of the gasoline/diesel/natural gas samples, the average of all subsequent vehicles/samples is taken. The purpose of averaging twice ensures that some vehicles are not weighed more than others based on sample abundance.

Gasoline exhaust

The fleet gasoline exhaust was determined to have a $\delta^{13}\text{C}$ value of $-27.27 (\pm 0.93) \text{‰}$ and a $\delta^{18}\text{O}$ value of $-12.46 (\pm 3.45) \text{‰}$ (Table 2). Two factors explain the variability of samples. For $\delta^{13}\text{C}$, gasoline comes from different suppliers, which have fuels from different geographic origin and hence isotopic signatures might slightly vary (Bush et al., 2007). Secondly, in British Columbia gasoline can be a blend of up to 10% bioethanol, which also affects the isotopic composition. For $\delta^{18}\text{O}$, it is important to know that cars built before 1988 (CAR003) are not required to have a catalytic converter in British Columbia (after 1988 a three way catalytic converter is mandatory by law), and effectiveness of the catalytic converters may affect the $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ values for CAR017, CAR020, and the motorbike (MTB001) are substantially lower than the rest of the fleet and comparable to the values obtained from diesel vehicles (Table 3).

Table 2: The average, maximum, and minimum values obtained from gasoline vehicle exhaust w.r.t. VPD-CO₂. The ‘number of replicates’ refers to the number of bags analyzed from this particular vehicle. Based on individual vehicles, the fleet total average $\delta^{13}\text{C}$ and total average $\delta^{18}\text{O}$, as well as the standard deviation for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are noted at the bottom of the table.

Vehicle ID	Number of Replicates	Average of corrected end member $\delta^{13}\text{C}(\text{‰})$	Max of corrected end member $\delta^{13}\text{C}(\text{‰})$	Min of corrected end member $\delta^{13}\text{C}(\text{‰})$	Average of corrected end member $\delta^{18}\text{O}(\text{‰})$	Max of corrected end member $\delta^{18}\text{O}(\text{‰})$	Min of corrected end member $\delta^{18}\text{O}(\text{‰})$
CAR001	6	-27.90	-27.74	-28.06	-14.96	-13.63	-15.86
CAR002	3	-27.83	-27.56	-28.00	-13.25	-12.01	-15.42
CAR003 ^(a)	3	-27.28	-27.22	-27.33	-18.42	-18.11	-18.85
CAR004	3	-27.95	-27.84	-28.02	-10.72	-10.17	-11.63
CAR005	3	-28.69	-28.35	-28.86	-13.36	-13.07	-13.63
CAR006	2	-27.70	-27.46	-27.94	-13.44	-12.99	-13.88
CAR008	4	-27.43	-27.36	-27.47	-14.19	-12.49	-15.87
CAR010	1	-27.24	-27.24	-27.24	-10.75	-10.75	-10.75
CAR013	2	-27.35	-27.33	-27.37	-11.90	-11.89	-11.90
CAR015	2	-26.78	-26.76	-26.80	-8.41	-8.22	-8.60
CAR016	1	-27.51	-27.51	-27.51	-14.47	-14.47	-14.47
CAR017	2	-28.47	-28.32	-28.62	-19.41	-19.33	-19.48
CAR019	2	-27.00	-26.95	-27.06	-12.16	-12.01	-12.30
CAR020	2	-27.12	-27.06	-27.19	-18.20	-18.15	-18.25
CAR021	2	-27.28	-27.10	-27.46	-8.46	-8.38	-8.54
CAR022	2	-27.26	-27.12	-27.40	-11.29	-11.08	-11.49

CAR023	4	-26.45	-26.22	-26.69	-9.00	-8.79	-9.17
CAR024	1	-27.05	-27.05	-27.05	-10.73	-10.73	-10.73
CAR028	2	-27.00	-26.95	-27.04	-9.42	-9.40	-9.43
CAR029	2	-25.13	-25.12	-25.15	-8.95	-8.72	-9.19
CAR031	2	-24.74	-24.71	-24.77	-6.32	-6.27	-6.36
MTB001	1	-28.74	-28.74	-28.74	-16.40	-16.40	-16.40
Fleet average		-27.27	Min: -28.74	Max: -24.77	-12.46	Min: -19.33	Max: -6.36
Standard Deviation		0.93			3.45		

^(a)This vehicle, built in 1954, has no catalytic converter only a muffler (all other cars are age 1988 or younger and have catalytic converters).

Diesel exhaust

The fleet average for diesel vehicles exhibited a slightly lower $\delta^{13}\text{C}$ of -28.81 (± 0.40) ‰ and substantially lower $\delta^{18}\text{O}$ of -18.63 (± 0.72) ‰ (Table 3).

Table 3: The average, maximum, and minimum values obtained from exhaust sampling for **diesel** vehicles w.r.t. VPD-CO₂. The ‘number of replicates’ refers to the number of bags analyzed from this particular vehicle. Based on individual vehicles, the fleet total average $\delta^{13}\text{C}$ and total average $\delta^{18}\text{O}$, as well as the standard deviation for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are noted at the bottom of the table.

Vehicle ID	Number of Replicates	Average of corrected end member $\delta^{13}\text{C}$ (‰)	Max of corrected end member $\delta^{13}\text{C}$ (‰)	Min of corrected end member $\delta^{13}\text{C}$ (‰)	Average of corrected end member $\delta^{18}\text{O}$ (‰)	Max of corrected end member $\delta^{18}\text{O}$ (‰)	Min of corrected end member $\delta^{18}\text{O}$ (‰)
BUS001	2	-28.94	-28.87	-29.00	-18.00	-17.92	-18.08
BUS002	2	-28.23	-28.13	-28.34	-17.61	-17.52	-17.71
BUS003	2	-28.81	-28.74	-28.88	-18.11	-18.01	-18.21
BUS004	2	-28.48	-28.45	-28.51	-17.51	-17.50	-17.53
CAR007	4	-28.56	-28.48	-28.71	-18.70	-18.55	-18.86
CAR009 ^(a)	2	-27.95	-27.83	-28.07	-19.04	-18.90	-19.19
CAR011	1	-29.29	-29.29	-29.29	-19.15	-19.15	-19.15
CAR012	2	-29.09	-29.07	-29.12	-18.28	-18.25	-18.32
CAR014	2	-28.77	-28.77	-28.77	-18.77	-18.76	-18.79
CAR018	2	-29.00	-28.85	-29.16	-19.90	-19.82	-19.98
CAR025	2	-29.21	-29.17	-29.25	-19.64	-19.47	-19.80
CAR026	2	-29.17	-29.11	-29.22	-18.73	-18.70	-18.76
CAR027	2	-29.08	-29.07	-29.09	-18.79	-18.75	-18.82
Fleet average		-28.81	Min: -27.83	Max: -29.29	-18.63	Min: -17.50	Max: -19.98
Standard Deviation		0.40			0.72		

^(a)Vehicle fueled with ‘biodiesel’ that contains up to 5% bioethanol

Natural gas exhaust

For natural gas, the average $\delta^{13}\text{C}$ value was $-41.64 (\pm 0.82)\text{‰}$, while the average $\delta^{18}\text{O}$ value was $-22.74 (\pm 0.56)\text{‰}$. The results show that there is little change in the isotopic composition of natural gas over the duration of observations.

Table 4: The average, maximum, and minimum values obtained from exhaust sampling for **natural gas** exhaust samples w.r.t. VPD-CO₂. The ‘number of replicates’ refers to the number of bags analyzed from this particular vehicle. Based on individual vehicles, the fleet total average $\delta^{13}\text{C}$ and total average $\delta^{18}\text{O}$, as well as the standard deviation for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are noted at the bottom of the table.

Sample ID	Number of Replicates	Average of corrected end member $\delta^{13}\text{C}$ (‰)	Max of corrected end member $\delta^{13}\text{C}$ (‰)	Min of corrected end member $\delta^{13}\text{C}$ (‰)	Average of corrected end member $\delta^{18}\text{O}$ (‰)	Max of corrected end member $\delta^{18}\text{O}$ (‰)	Min of corrected end member $\delta^{18}\text{O}$ (‰)
NG002	2	-42.22	-42.19	-42.25	-23.41	-23.39	-23.42
NG003	1	-41.75	-41.75	-41.75	-23.43	-23.43	-23.43
NG004	2	-41.48	-41.42	-41.54	-23.09	-22.93	-23.25
NG005	1	-41.18	-41.18	-41.18	-23.25	-23.25	-23.25
NG006	1	-41.46	-41.46	-41.46	-23.34	-23.34	-23.34
NG007	2	-40.38	-40.34	-40.42	-22.27	-22.20	-22.34
NG008	2	-39.98	-39.92	-40.03	-21.90	-21.74	-22.06
NG009	1	-40.37	-40.37	-40.37	-21.68	-21.68	-21.68
NG010	2	-41.88	-41.82	-41.94	-23.22	-23.14	-23.31
NG011	1	-42.30	-42.30	-42.30	-22.47	-22.47	-22.47
NG012	2	-42.46	-42.44	-42.48	-22.76	-22.75	-22.76
NG013	2	-41.92	-41.92	-41.92	-22.18	-22.12	-22.24
NG014	2	-42.35	-42.33	-42.36	-22.62	-22.52	-22.73
NG015	2	-42.31	-42.17	-42.46	-22.89	-22.55	-23.24
NG016	2	-42.48	-42.46	-42.51	-22.85	-22.84	-22.85
Average		-41.64	Min: -39.92	Max: -42.51	-22.74	Min: -21.68	Max: -23.43
Standard Deviation		0.82			0.56		

Conclusions

The variation of $\delta^{13}\text{C}$ values of all three fossil fuel types are relatively narrow and depend on fuel type (see Figure 4). In contrast, the $\delta^{18}\text{O}$ values vary significantly for gasoline likely due to types and efficiency of convertors (Schumacher et al., 2011). The $\delta^{18}\text{O}$ values for CAR003 (no converter), CAR017, CAR020, and the motorbike (MTB001) are clearly lower than the rest of the fleet and comparable to the values obtained from diesel vehicles and predicted for unfractionated combustion ($\delta^{18}\text{O} = -17\text{‰}$, Schumacher et al., 2011). For both, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, natural gas is well separated from diesel and gasoline, although it is currently unclear why $\delta^{18}\text{O}$ is significantly lower than the unfractionated prediction. Schumacher et al., 2011 suggest that fires with an unlimited O₂ availability such as the current gas torch, could also include a diffusive step in the supply of oxygen which might question the unfractionated prediction and lower $\delta^{18}\text{O}$ of the produced CO₂.

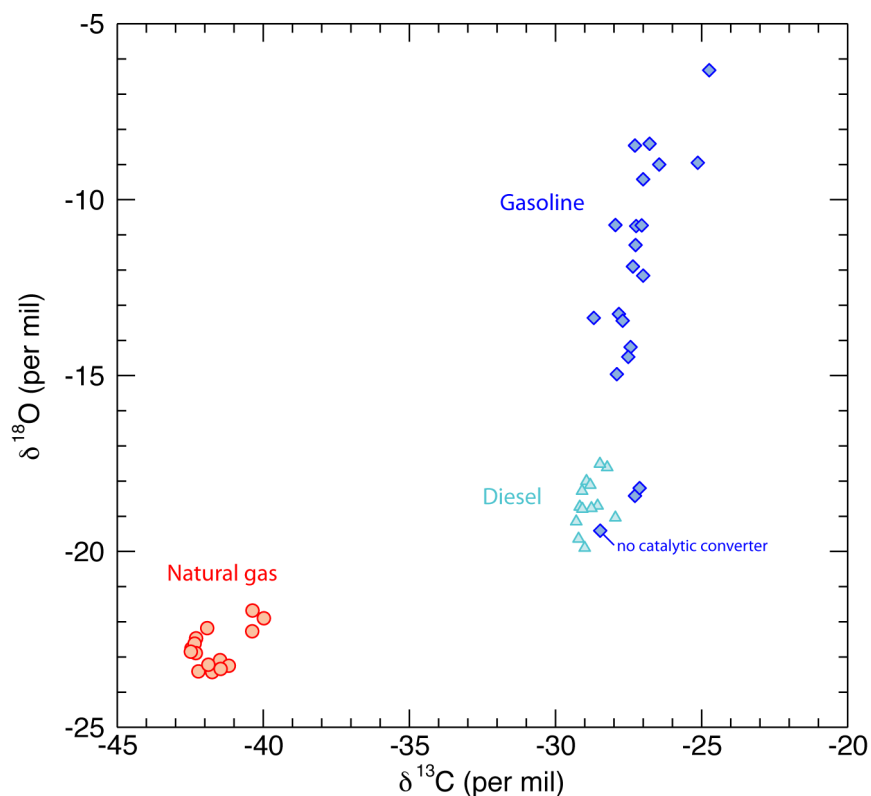


Figure 4: All samples in $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ space. Samples shown are corrected for background air influence.

Analytical errors were reduced by only accepting samples which met the strict standards imposed during the analysis such as the required reproducibility of the 2 cycles. However, it is possible that errors may still have been introduced during the sampling and dilution process. Occasionally small amounts of

water would condense in the sampling tube, which may have caused temporary H₂O-CO₂ isotope exchanges.

Urban atmospheric CO₂ originates from numerous sources, one of which being the combustion of fossil fuels. By utilizing the isotopic signatures of CO₂ reported here, the degree to which different sources contribute to the overall abundance could be examined using mixing models. This study determined the typical isotopic composition of CO₂ emitted from gasoline burning vehicles, diesel burning vehicles, and natural gas burning in Vancouver, BC, between November 2013 and May 2014. For a complete picture, source characteristics for soil, plant and human respiration are needed and reported in a different study.

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Appendix - Sampled vehicles

Car ID	Fuel type	Vehicle manufacturer model	Year built	Date samples taken
BUS-01	Diesel	(TranslinkPassenger Bus)	2009	2014-04-25
BUS-02	Diesel	(TranslinkPassenger Bus)	1998	2014-04-25
BUS-03	Diesel	(TranslinkPassenger Bus)	2009	2014-04-25
BUS-04	Diesel	(TranslinkPassenger Bus)	2000	2014-04-25
CAR001	Gasoline	Dodge Caravan	2006	2013-11-12
CAR002	Gasoline	Toyota Tacoma	2006	2013-11-12
CAR003	Gasoline	Ford F-100 pickup	1954	2013-11-12
CAR004	Gasoline	Mazda Protoge 5	2002	2013-11-13
CAR005	Gasoline	Volvo V50	2006	2013-11-13
CAR006	Gasoline	Toyota Prius	2010	2013-11-14
CAR007	Diesel	Ford F-350		2013-11-19
CAR008	Gasoline	Dodge Caravan	2006	2013-11-19
CAR009	Biodiesel	Dodge Sprinter		2013-11-19
CAR010	Gasoline	Ford transit		2014-02-14
CAR011	Diesel	–	2006	2014-02-14
CAR012	Diesel	RTV900	2008	2014-02-14
CAR013	Gasoline	Ford Transit	2013	2014-02-14
CAR014	Diesel	Dodge Sprinter	2006	2014-02-14
CAR015	Gasoline	Ford Transit	2010	2014-02-14
CAR016	Gasoline	Honda Civic		2014-03-07
CAR017	Gasoline	Chevrolet 1 ton Cube	1994	2014-03-14
CAR018	Diesel	GMC W4500		2014-03-14
CAR019	Gasoline	Chevrolet 1 ton Cube	1994	2014-03-14
CAR020	Gasoline	Chevrolet 1 ton Cube	1994	2014-03-14
CAR021	Gasoline	Ford Transit Connect	2010	2014-03-14
CAR022	Gasoline	Ford F-450		2014-03-14
CAR023	Gasoline	Toyota Tundra	2014	2014-03-14
CAR024	Gasoline	Chevrolet S-10	1993	2014-03-21
CAR025	Diesel	Mercedes Sprinter Bluetech 2500	2000	2014-03-21
CAR026	Diesel	Dodge Sprinter 3599	2000	2014-03-21
CAR027	Diesel	Ford LCF		2014-03-21
CAR028	Gasoline	Chevrolet S-10	1993	2014-03-21
CAR029	Gasoline	Ford Ranger	2005	2014-05-05
CAR030	Gasoline	Mazda 3	2012	2014-05-05
CAR031	Gasoline	Toyota RAV 4	2008	2014-05-05
MTB001	Gasoline	Triumph Street Triple 2012 (Motorbike)	2012	2013-11-13