



## Carbon isotopic characterization of formaldehyde emitted by vehicles in Guangzhou, China



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### HIGHLIGHTS

- Carbon isotopic ratio of formaldehyde (HCHO) emitted from in-use vehicles and stand-alone engines was measured.
- Both production and consumption processes in vehicle engine combustion cylinder influenced the HCHO carbon isotopic ratio.
- The catalytic converter provided additional consumption process.
- The HCHO emission factor was higher than those in previous studies.
- HCHO directly emitted from vehicle was the major source in a bus station in Guangzhou, South China.

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### ABSTRACT

Formaldehyde (HCHO) is the most abundant carbonyl compound in the atmosphere, and vehicle exhaust emission is one of its important anthropogenic sources. However, there is still uncertainty regarding HCHO flux from vehicle emission as well as from other sources. Herein, automobile source was characterized using HCHO carbon isotopic ratio to assess its contributions to atmospheric flux and demonstrate the complex production/consumption processes during combustion in engine cylinder and subsequent catalytic treatment of exhaust. Vehicle exhausts were sampled under different idling states and HCHO carbon isotopic ratios were measured by gas chromatograph–combustion–isotopic ratio mass spectrometry (GC–C–IRMS). The HCHO directly emitted from stand-alone engines (gasoline and diesel) running at different load was also sampled and measured. The HCHO carbon isotopic ratios were from  $-30.8$  to  $-25.7\text{‰}$  for gasoline engine, and from  $-26.2$  to  $-20.7\text{‰}$  for diesel engine, respectively. For diesel vehicle without catalytic converter, the HCHO carbon isotopic ratios were  $-22.1 \pm 2.1\text{‰}$ , and for gasoline vehicle with catalytic converter, the ratios were  $-21.4 \pm 0.7\text{‰}$ . Most of the HCHO carbon isotopic ratios were heavier than the fuel isotopic ratios (from  $-29$  to  $-27\text{‰}$ ). For gasoline vehicle, the isotopic fractionation ( $\Delta^{13}\text{C}$ ) between HCHO and fuel isotopic ratios was  $7.4 \pm 0.7\text{‰}$ , which was higher than that of HCHO from stand-alone gasoline engine ( $\Delta^{13}\text{C}_{\text{max}} = 2.7\text{‰}$ ), suggesting additional consumption by the catalytic converter. For diesel vehicle without catalytic converter,  $\Delta^{13}\text{C}$  was  $5.7 \pm 2.0\text{‰}$ , similar to that of stand-alone diesel engine. In general, the carbon isotopic signatures of HCHO emitted from automobiles were not sensitive to idling states or to other vehicle parameters in our study condition. On comparing these HCHO carbon isotopic data with those of past studies, the atmospheric HCHO in a bus station in Guangzhou might mainly come from vehicle emission for the accordance of carbon isotopic data.

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### 1. Introduction

Formaldehyde (HCHO) has been identified as a toxic air pollutant, known to cause adverse health effects (USEPA, 1990). In addition, it also plays a crucial role in photochemical reactions

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influencing smog processes in the atmosphere (Grosjean and Grosjean, 1997). Therefore, scientists are more interested in examining this compound. The primary sources of HCHO in the atmosphere are emission from vehicle exhaust (Ho et al., 2007; Hoekman, 1992; Viskari et al., 2000), biogenic emissions (Guo et al., 2009; Martin et al., 1999) and biomass burning (Hays et al., 2002), whereas the secondary source is photo-oxidation of atmospheric volatile organic compounds (Ho and Yu, 2002; Possanzini et al., 2002).

In the study of atmospheric chemistry, determination of isotopic composition of atmospheric trace gases is useful for source identification and elucidation of various important processes that cannot be ascertained from concentration measurements alone (Keppler et al., 2004; Rudolph and Czuba, 2000; Rudolph et al., 2002; Yamada et al., 2005). Furthermore, isotopic composition measurement can also be used to assess the flux of many atmospheric compounds (Goldstein and Shaw, 2003; Wang et al., 2012). In previous studies, carbon isotopic compositions of ambient HCHO in different sites were reported, and the primary results showed that carbon isotopic analysis could provide some valuable information for better understanding of the sources of HCHO in ambient air (Brenninkmeijer et al., 2003; Johnson and Dawson, 1990; Rice and Quay, 2009; Tanner et al., 1996; Wen et al., 2005). However, information on the isotopic signature of the sources needed for interpretation of atmospheric HCHO is limited (Guo et al., 2009; Wen et al., 2005). Hence, more source emission data are needed for the interpretation or modeling of stable carbon isotopic ratios of HCHO in the atmosphere.

Vehicular emission is a major source of urban air pollutants such as nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO), volatile organic compounds (VOCs) (Ban-Weiss et al., 2008; Ho and Yu, 2002; Possanzini et al., 2002), and fine particles (Fraser et al., 1998; Schauer et al., 2002), and its environmental and health effects are of concern. Therefore, numerous studies particularly focused on vehicle emissions have been carried out. HCHO is the most abundant carbonyl compound found in vehicle exhaust (Ban-Weiss et al., 2008; Ho et al., 2007; Schauer et al., 2002). In previous studies, a compound-specific carbon isotopic analysis method for atmospheric HCHO had been developed (Yu et al., 2006). Using this method, the present study firstly reported the measurement of HCHO carbon isotopic ratio directly emitted from vehicle using gasoline and diesel vehicles with varying ages and mileages, and under different operational modes while idling. As neither air nor fuel in the vehicles was found to contain significant HCHO, any HCHO present in the exhaust was considered to have been formed by the combustion process (Wagner and Wyszynski, 1996). To further explore the emission characteristics, gasoline and diesel engines running on a dynamometer were used to assess the effect of loading.

## 2. Materials and methods

### 2.1. Materials

Chloroform purchased from Shantou Xilong Chemical Co., Ltd was distilled thrice, and 2, 4-dinitrophenylhydrazine (DNPH) purchased from Fluka was recrystallized twice in high-performance liquid chromatography (HPLC)-grade acetonitrile (ACN; purchased from Merck). Cysteamine hydrochloride was purchased from Fluka, and sodium bisulfite ( $\text{NaHSO}_3$ ) was purchased from United Research Institute of Chengdu. The sampling medium was a Sep-Pak Silica Gel Cartridge (Waters). For HCHO concentration analysis, the cartridges coated with DNPH, as previously reported (Feng et al., 2004, 2005), were used, and for carbon isotopic analysis, the cartridges coated with  $\text{NaHSO}_3$  were

employed to collect HCHO (Yu et al., 2006). For the measurement of  $\text{CO}_2$  and CO concentration in the vehicle exhaust, an AUTO5-1 (KANE, UK) analyzer was used.

### 2.2. Sampling details

Five light-duty gasoline-powered passenger cars with three-way functional catalytic converters (labeled A–E) and eight diesel-powered trucks without catalytic converter (labeled H–O) in use in Guangzhou, South China, were tested at idling condition under different start modes in July and November 2008, respectively. Throughout this study, the term “idling” indicates that the vehicle was parked while the engine was rotating. The vehicles were run in two different start modes: 1) cold start mode (sampling was started immediately after starting up and the vehicle was parked for several hours), in which the vehicle was only run at low engine rotation speed to prevent engine damage and 2) hot start mode (sampling was started after the engine and catalysts were heated by a test run), in which both low and high engine rotation speed were chosen for sampling. All the vehicles were equipped with an electronic fuel injection system, and other relevant details of the tested vehicles are presented in Table 1. Copper tubes coated with KI were placed into the vehicle exhaust tailpipe. The Sep-Pak cartridges coated with  $\text{NaHSO}_3$  (for HCHO carbon isotopic ratio analysis) and DNPH (for HCHO concentration analysis) were attached to the copper tubes, respectively. The sampling flow was regulated with an adjustable flow controller at a flow rate of 1–1.5  $\text{L min}^{-1}$ , and the sampling time for each sample was about 5–10 min. After collection, the cartridge samples were stored at 4 °C until extraction. For the detection of  $\text{CO}_2$  and CO concentration, the AUTO5-1 sample detector was also placed into the tailpipe and measurements were carried out. To measure the fuel  $\delta^{13}\text{C}$  value, the diesel fuel was collected from each truck's diesel tank, while the gasoline samples were randomly collected from eight gas stations in Guangzhou, because collection of samples directly from the gasoline tank of the vehicles was prohibited.

The stand-alone engine tests were conducted in April 2009. For gasoline engine, the tests were conducted at Guangzhou Mechanical Engineering Research Institute, and a gasoline-fueled engine (type DH491Q) was chosen to examine the effect of loading on the isotopic composition of HCHO. The fuel used in the engine tests was commercial Chinese in-use 93<sup>#</sup> gasoline fuel. The engine was simulated at different loads on a direct-current dynamometer with an FC2000 engine automatic control system. The exhaust from the engine was discharged through a metal tailpipe and then sampled by DNPH- and  $\text{NaHSO}_3$ -coated Sep-Pak cartridges. The DH491Q engine had four cylinders and no catalytic converter for exhaust treatment, and its rated power was 70 kW at 4500 rpm. The engine was run at 0, 25, 50, 75, and 100% of full load at a constant speed of 2500 rpm (at idling state, a speed of 770 rpm with no load was employed). As the engine cylinder reaction temperature was not available, the exhaust temperature, automatically recorded by the detector of FC2000 engine control system at a distance of 20 cm from the cylinder's exhaust manifold, was used to reflect the engine cylinder temperature.

Furthermore, a DL190-12 diesel engine with no catalytic converter was used at the College of Mechanical and Electrical Engineering of Guangdong University of Technology. The bore and stroke were 90 and 110 mm, respectively. The displacement volume was 0.7 L and the compression ratio of the engine was 18:1. The related power was 8.8 kW at 2200 rpm. During the experiment, constant speed (1200 rpm) and varying engine loads (0, 20, 40, 60, 80, 100% of full load) were used (at idling state, a speed of 650 rpm with no load was employed). The exhaust temperature was

**Table 1**  
Details of gasoline and diesel vehicles tested in this study.

Vehicle ID	Manufacturer	Model	Fuel	Cylinder number	Displacement volume (L)	Engine power (kW)	Used years	Catalytic converter	Odometer (km)	Curb weight (kg)
A	Honda	Accord	Gasoline	4	2.3	/	6.0	Yes	110,000	/
B	Honda	Accord	Gasoline	4	2.3	/	6.5	Yes	193,000	/
C	Honda	Accord	Gasoline	4	2.0	/	5.0	Yes	60,000	/
D	Honda	Civic	Gasoline	4	2.0	/	4.0	Yes	136,000	/
E	Mazda	Premacy	Gasoline	4	1.8	/	2.5	Yes	63,400	/
H	Dongfeng	Xiaojinba	Diesel	4	/	70	0.5	No	7646	3600
I	Dongfeng	Xiaobawang	Diesel	4	/	68	5.0	No	400,000	3300
J	JAC	Shuailing	Diesel	4	/	68	1.0	No	50,000	3300
K	JAC	Shuailing	Diesel	4	/	68	4.0	No	200,000	3300
L	Foton	Ollin	Diesel	4	/	88	2.0	No	80,000	5000
M	Faw	Jiefang	Diesel	4	/	88	0.25	No	13,000	5000
N	Foton	Ollin	Diesel	4	/	88	1.5	No	50,000	5000
O	Dongfeng	Xiaobawang	Diesel	4	/	68	4.0	No	18,000	3300

measured by the detector about 50 cm away from the cylinder's exhaust manifold, and the exhausts were sampled by DNPH- and NaHSO<sub>3</sub>-coated Sep-Pak cartridges, as described earlier.

### 2.3. Sample pretreatment and instrumental analysis

The methods for sample pretreatment, HPLC, and isotopic analyses have been described elsewhere in detail (Feng et al., 2004; Yu et al., 2006). Cartridges collection efficiency was determined with two cartridges in series, and over 99% of formaldehyde was found in the first cartridge. Briefly, for HCHO concentration analysis, the DNPH-coated cartridges were eluted with 2 mL of ACN and prepared for HPLC measurement. For HCHO carbon isotopic measurement, the NaHSO<sub>3</sub>-coated cartridges were firstly eluted with 5 mL of pure water. Then the solution was adjusted to pH 2, heated using a water bath to 60 °C for 20 min. Subsequently, the solution was adjusted to pH 8–9, and 150 µL of cysteamine aqueous solution was added. After 4 h, the solution was extracted thrice with chloroform, and the combined extract was dried over anhydrous sodium sulfate, filtered and blown down to 100 µL using a gentle flow of high-purity N<sub>2</sub>.

The δ<sup>13</sup>C values of cysteamine hydrochloride, gasoline, and diesel fuel were measured using an elemental analyzer/isotope ratio mass spectrometer (EA/IRMS, DELTA<sup>plus</sup>XL mass spectrometer, Thermo Finnigan, Bremen, Germany). Isotopic standardization was accomplished using black carbon with known δ<sup>13</sup>C value (δ<sup>13</sup>C = −29.70‰). The uncertainty of measurement results was ±0.3‰. The δ<sup>13</sup>C values of HCHO-cysteamine derivative (thiazolidine) were measured using the gas chromatograph–combustion–isotopic ratio mass spectrometry (GC/C/IRMS) system (HP 6890 GC system, Agilent, USA) coupled to a combustion furnace and an isotope ratio mass spectrometer (Isoprime II, GV Instruments, UK). The GC was equipped with a ZB-XLB column (30 m × 0.32 mm × 0.25 µm, Phenomenex, USA), and the oven temperature program was set to 50 °C at the start, and then increased to 85 °C at 3 °C min<sup>−1</sup> and 290 °C (held for 10 min) at 20 °C min<sup>−1</sup>. Helium was used as the carrier gas at flow rate of 1 mL min<sup>−1</sup>. The combustion interface was operated at 980 °C. Reoxidation was performed once a day for about 30 min. The reproducibility and accuracy of carbon isotopic analyses were evaluated routinely every day using 10 laboratory isotopic standards (C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>20</sub>, C<sub>22</sub>, C<sub>25</sub>, C<sub>28</sub>, C<sub>30</sub>, and C<sub>32</sub> *n*-alkanes supplied by Indiana University) with predetermined isotopic values (Yu et al., 2006). The corresponding standard deviation and the deviation between the measured data and predetermined data were all below 0.5‰. The measurements were made in triplicate for every sample.

### 2.4. Determination of HCHO carbon isotopic ratio and analytic error

Based on the kinetic isotope effect, if no isotope fractionations occurred during the derivatization process, the carbon isotopic compositions of HCHO, its derivative (thiazolidine), and derivative reagent (cysteamine) should comply with the following mass balance equation (Yu et al., 2006):

$$\delta^{13}\text{C}_{\text{thiazolidine}} = f_{\text{HCHO}}\delta^{13}\text{C}_{\text{HCHO}} + f_{\text{cysteamine}}\delta^{13}\text{C}_{\text{cysteamine}} \quad (1)$$

where  $f_{\text{HCHO}}$  and  $f_{\text{cysteamine}}$  are the mole fractions of the carbon atom in thiazolidine arising from the underivatized HCHO and cysteamine reagent, respectively. In this study, the value of  $f_{\text{HCHO}}$  was 1/3 and that of  $f_{\text{cysteamine}}$  was 2/3. The analytic error of the calculated (or predicted) data for underivatized HCHO (usually expressed as the standard deviation,  $S$ ), was calculated by using the following equation:

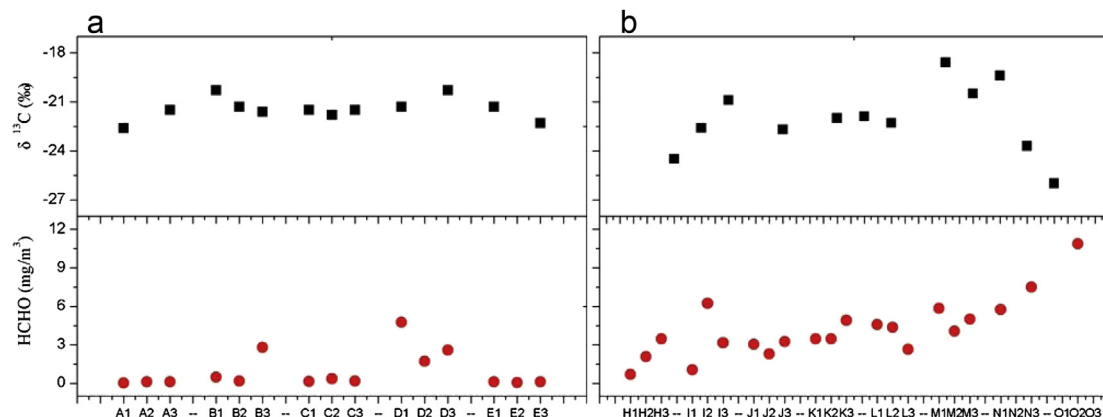
$$S_{\text{HCHO}}^2 = (1/f_{\text{HCHO}})^2 S_{\text{thiazolidine}}^2 + (f_{\text{cysteamine}}/f_{\text{HCHO}})^2 S_{\text{cysteamine}}^2 \quad (2)$$

Previous studies have shown that the predicted and measured δ<sup>13</sup>C values of HCHO derivative agreed well within the precision limits of the GC/C/IRMS measurements (Guo et al., 2009; Yu et al., 2006). The results obtained demonstrated that no carbon isotopic fractionation occurred during sample pretreatment and that this method was effective for measuring the δ<sup>13</sup>C value of HCHO in the atmosphere. For these measurements, the calculated standard deviation of HCHO was 0.1–1.6‰, which was greater than the measured standard deviation of its derivative (mostly <0.5‰), because there was only one carbon atom in the HCHO molecule and the analytic deviation increased during the calculation process using Eq. (2).

## 3. Results and discussion

### 3.1. HCHO concentrations and carbon isotopic ratios obtained from vehicle test

In Fig. 1, the HCHO carbon isotopic ratios measured at each sampling point in the vehicle exhaust experiment were shown, together with their corresponding concentrations. The <sup>13</sup>C values of HCHO emitted from vehicles remained nearly constant [(average and 1 SD) −21.4 ± 0.7 and −22.1 ± 2.1‰ for gasoline and diesel vehicle, respectively], and were all heavier than those of the fuel (about −28‰). An important factor controlling the variation in δ<sup>13</sup>C



**Fig. 1.** Concentrations and carbon isotopic ratios of HCHO emitted from vehicles (a: gasoline vehicle; b: diesel vehicle; A–O: label of the vehicle; 1: cold start at low rotation speed of 600 rpm; 2: hot start at low rotation speed of 600 rpm; 3: hot start at high rotation speed of 5000 and 2000 rpm for gasoline and diesel vehicle, respectively).

of HCHO emitted from vehicles might be the variation in  $\delta^{13}\text{C}$  of the fuel. In this study, the fuel  $\delta^{13}\text{C}$  values varied just 2‰ (from  $-29$  to  $-27$ ‰). However, for other regions, the range of the values might be different. The stable carbon isotopic ratio for crude oil worldwide were approximately from  $-23$  to  $-34$ ‰, with most of the crude oils having  $\delta^{13}\text{C}$  values between  $-26$  and  $-32$ ‰ (Yeh and Epstein, 1981). Although our data fall in this range, the different values reported in other studies might be due to the different fuel compositions in other places. Literature results showed that HCHO was always the predominant aldehyde emitted by automobiles (Ho et al., 2007; Possanzini et al., 2002; Schauer et al., 2002). Noting the small variation in the  $\delta^{13}\text{C}$  value of local fuel, our measured  $\delta^{13}\text{C}$  value for HCHO should be representative of those emitted from light-duty gasoline vehicles and diesel trucks running in South China.

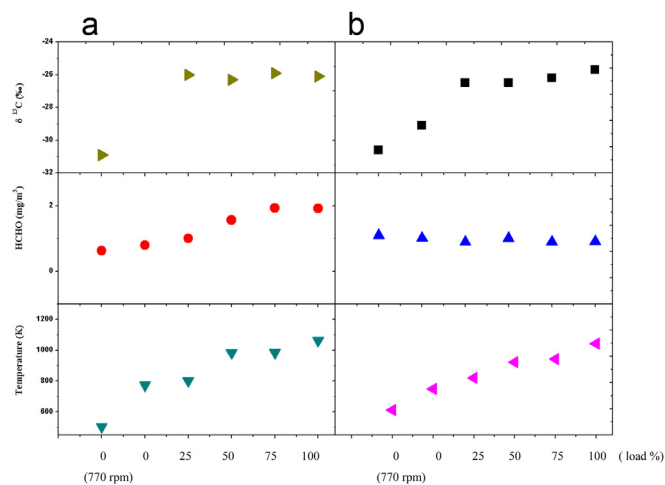
With regard to the HCHO concentrations in the vehicle exhaust, the variation was  $0.03$ – $4.8$  and  $0.7$ – $10.9$   $\text{mg m}^{-3}$  for gasoline- and diesel-powered vehicle, respectively. The variation in the HCHO concentration was several times higher for diesel-powered vehicle without catalytic converter. Furthermore, no obvious dependence of HCHO carbon isotopic ratios on their concentrations was observed.

### 3.2. HCHO concentrations and carbon isotopic ratios obtained from engine test

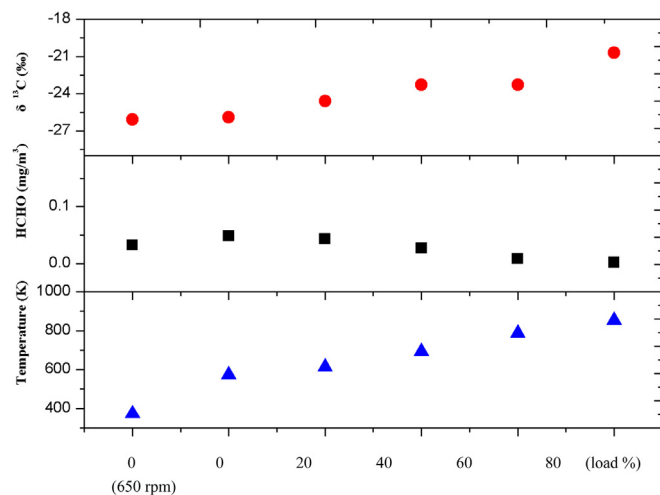
Figs. 2 and 3 showed the exhaust temperatures, HCHO concentrations, and carbon isotopic ratios at different engine loads (in % of the full load). For gasoline-powered engine, two parallel tests were conducted, and the data obtained were shown in Fig. 2. Even under the control of the FC2000 system and under similar operation parameters, different HCHO concentration data and trends were obtained. The HCHO concentration was influenced by a complex process, and it was not easy to achieve a regular pattern. However, with regard to the temperature of the engine exhaust, the data measured at each point were positively correlated with the load of the engine. Thus, increase in load could be expressed as an increase in exhaust temperature. Furthermore, the HCHO carbon isotopic ratios were mostly positively correlated with the temperature of the engine exhaust. The concentration of HCHO directly emitted from engine had no obvious dependence on the HCHO carbon isotopic ratios.

### 3.3. Isotopic fractionation during the combustion process in engine

Isotopic fractionation of hydrocarbons is observed during biosynthesis and biomass burning (Keppler et al., 2004; Yamada



**Fig. 2.** Engine exhaust temperature, HCHO concentration, and carbon isotopic ratio versus engine load in two parallel gasoline engine tests a and b (engine rotation speed = 2500 rpm,  $\delta^{13}\text{C}$  of fuel =  $-28.4 \pm 0.5$ ‰).



**Fig. 3.** Engine exhaust temperature, HCHO concentration, and carbon isotopic ratio versus engine load in diesel engine test (engine rotation speed = 1200 rpm,  $\delta^{13}\text{C}$  of fuel =  $-28.4 \pm 0.3$ ‰).

et al., 2009). During the combustion process, two different types of isotopic fractionation occur: production and consumption (Czapiewski et al., 2002). Compounds containing  $^{13}\text{C}$  possess lower zero-point energies, hence, activation energies and enthalpies for reactions involving  $^{13}\text{C}$  are generally higher. Then  $^{13}\text{C}$ -depleted HCHO is expected to exist if the production process dominates (mainly in low temperature),  $^{13}\text{C}$ -enriched HCHO would be predominant in high temperature for the consumption process. As shown in Figs. 2 and 3, with temperature increasing, positive isotopic fractionation occurred and mostly became larger, which signifies the major effect of consumption process.

As mentioned earlier, two different types of isotopic fractionation occur during the combustion process in engine: production and consumption. For HCHO, these two processes might have possibly occurred at different rates and/or might have been nonlinear, and could have occurred sufficiently fast to cause isotopic fractionation. Therefore, it was not expected to get a good relationship between the concentration and the corresponding isotopic data.

#### 3.4. Additional isotopic fractionation in catalytic converter

To offset the influence of variations in  $\delta^{13}\text{C}_{\text{Fuel}}$ , the isotopic differences between  $\delta^{13}\text{C}_{\text{HCHO}}$  and  $\delta^{13}\text{C}_{\text{Fuel}}$ , which represent the apparent isotopic fractionation occurring during fuel burning, were calculated and expressed as  $\Delta^{13}\text{C}$  (‰), as defined by the following equation (Yamada et al., 2009):

$$\Delta^{13}\text{C}_{\text{HCHO-Fuel}} = \left\{ \frac{(\delta^{13}\text{C}_{\text{HCHO}} + 1000)}{(\delta^{13}\text{C}_{\text{Fuel}} + 1000)} - 1 \right\} \times 1000 \quad (3)$$

For the low values of  $\delta^{13}\text{C}_{\text{HCHO}}$  and  $\delta^{13}\text{C}_{\text{Fuel}}$ ,  $\Delta^{13}\text{C}_{\text{HCHO-Fuel}}$  could be approximately calculated as follows:

$$\Delta^{13}\text{C}_{\text{HCHO-Fuel}} = \delta^{13}\text{C}_{\text{HCHO}} - \delta^{13}\text{C}_{\text{Fuel}} \quad (4)$$

For gasoline engine test, the value of  $\Delta^{13}\text{C}$  was from  $-2.5$  to  $2.7$ ‰, and  $\Delta^{13}\text{C}_{\text{max}}$  was  $2.7$ ‰, indicating the largest isotopic fractionation under the combustion state in engine cylinder at the highest engine temperature. On the other hand, for diesel engine test, the value of  $\Delta^{13}\text{C}$  was from  $2.3$  to  $7.7$ ‰. As shown in Fig. 4,  $\Delta^{13}\text{C}$  was  $5.7 \pm 2.0$ ‰ for diesel vehicle, and  $7.4 \pm 0.7$ ‰ for

gasoline vehicle, respectively. The  $\Delta^{13}\text{C}$  value obtained in gasoline vehicle test was  $5$ ‰ larger than the  $\Delta^{13}\text{C}_{\text{max}}$  detected in gasoline engine test. The stand-alone gasoline engine employed in this study was a common commercial type used in cars, and the working condition reflected the running state of on-road cars. Thus, installation of catalytic converter in gasoline vehicle should be responsible for the difference in the  $\Delta^{13}\text{C}$  values. Catalytic converter has been reported to exhibit a high conversion efficiency of over  $90\%$  for aldehyde compounds (Shore et al., 1993), indicating additional HCHO consumption process in the exhaust. As discussed earlier, a positive isotopic fractionation would have occurred, and HCHO with enriched  $\delta^{13}\text{C}$  would have remained in the gasoline vehicle exhaust emitted from tailpipe, similar to that observed in the study of isotopic characterization of  $\text{N}_2\text{O}$  in the car exhaust (Toyoda et al., 2008). However, for diesel vehicle without catalytic converter, the values of  $\Delta^{13}\text{C}$  were close to those of stand-alone engine. On the other hand, when compared with the  $\Delta^{13}\text{C}$  values of these two types of vehicle, a slightly higher  $\Delta^{13}\text{C}$  value was detected for gasoline vehicle, which might be the effect of additional isotopic fractionation in catalytic converter.

#### 3.5. Effect of vehicular operation conditions

It has been reported that the  $\delta^{13}\text{C}$  values of non-methane hydrocarbons emitted from biomass burning were correlated with burning conditions (Czapiewski et al., 2002; Yamada et al., 2009). However, in the present study,  $\delta^{13}\text{C}$  of HCHO did not show a significant correlation with air-to-fuel ratios and combustion efficiency. This might be due to the high combustion efficiency (mostly  $> 99\%$ ) resulting from the effect of the electronic fuel injection system, which maintains a balanced air-to-fuel ratio for effective and controlled combustion by incorporating oxygen sensor to aid in feedback control of fuel injection ([http://en.wikipedia.org/wiki/Fuel\\_injection](http://en.wikipedia.org/wiki/Fuel_injection)). Furthermore, a balanced air-to-fuel ratio is also a required condition for effective catalytic conversion.

Meanwhile, non-parametric Mann–Whitney  $U$  test confirmed that there were no significant differences between the start modes (data not shown). Mileage and used years had only a weak influence on the isotopic values. This phenomenon could also be explained by the function of the electronic fuel injection system, which controls the amount of fuel injected to match the engine's dynamic needs for effective combustion under a wide range of operation conditions, such as start modes, engine load, engine temperature, and fuel octane level; as a result, the effects of mileage and used years on  $\delta^{13}\text{C}$  of HCHO were reduced.

Furthermore, with regard to the HCHO carbon isotopic ratios obtained for these two types of vehicle, more scattered data were found for diesel vehicle. A possible reason for this could be that during the long duration of sampling (5–10 min), the catalytic converter would have been totally activated and would have had a major effect on HCHO carbon isotopic ratios (as discussed earlier), resulting in more concentrated data. Thus, for diesel vehicle without additional consumption of catalytic converter, more scattered data were observed, indicating the influence of other factors (such as idling states, etc.).

#### 3.6. HCHO emission factor from vehicle exhaust

Together with the analysis of HCHO concentration and carbon isotopic ratio, the  $\text{CO}_2$  concentrations were measured simultaneously. The concentration proportion of HCHO/ $\text{CO}_2$  (both in mole concentration) was shown in Fig. 5. Based on the carbon balance method, the emission factors of HCHO were roughly calculated for

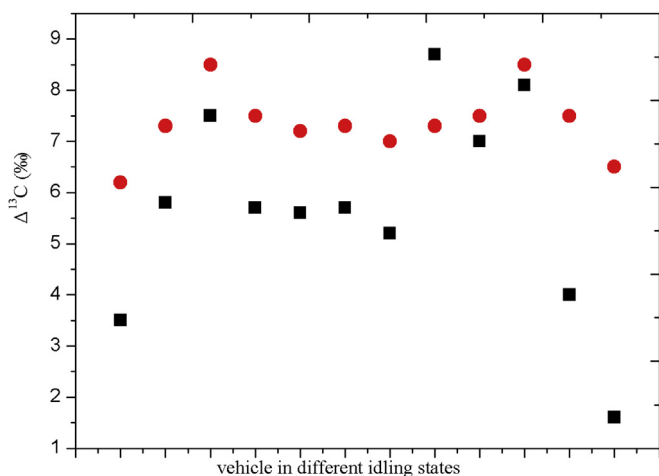


Fig. 4. Carbon isotopic fractionation ( $\Delta^{13}\text{C}$ , calculated by  $\delta^{13}\text{C}_{\text{HCHO}} - \delta^{13}\text{C}_{\text{fuel}}$ ) noted in vehicle test (square:  $\Delta^{13}\text{C}$  from diesel vehicle with average  $\pm$  SD =  $5.7 \pm 2.0$ ‰; circle:  $\Delta^{13}\text{C}$  from gasoline vehicle with average  $\pm$  SD =  $7.4 \pm 0.7$ ‰).

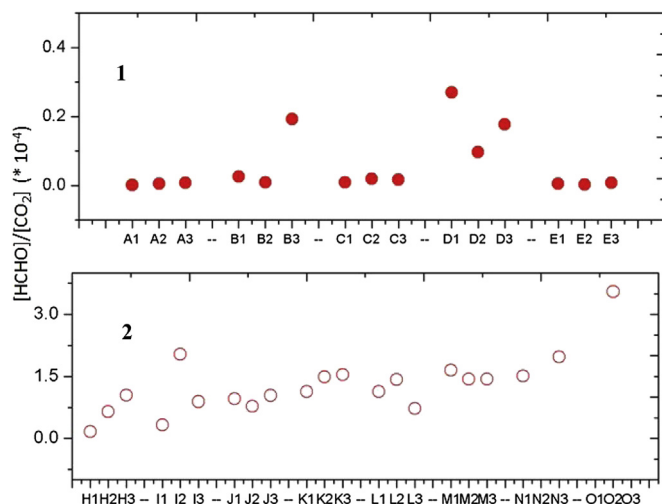


Fig. 5. HCHO/CO<sub>2</sub> ratios (in mole concentration) in vehicle exhaust. A–E, gasoline vehicle; H–O, diesel vehicle; 1:  $0.057 \pm 0.086$ ; 2:  $1.28 \pm 0.71$  ( $\times 10^{-4}$ , average  $\pm$  SD).

gasoline and diesel vehicle, respectively. The HCHO emission factor for diesel vehicle was  $320 \pm 176$  mg L<sup>-1</sup> (HCHO mass vs. fuel volume, presuming 85% carbon content and 0.85 kg L<sup>-1</sup> of diesel oil density) and that for gasoline vehicle was  $12 \pm 18$  mg L<sup>-1</sup> (presuming 85% carbon content and 0.72 kg L<sup>-1</sup> of gasoline oil density). On the other hand, for diesel vehicle without catalytic converter, the HCHO emission factor was tens of times higher. In previous studies, Kean et al. (2001) obtained an HCHO emission factor of 68 mg L<sup>-1</sup> for all carbonyl with 45% HCHO, whereas Grosjean et al. (2001) achieved an HCHO emission factor of 10–60 mg L<sup>-1</sup> (presuming oil consumption of 10–20 L/100 km). When compared with these data, those obtained in the present study are slightly higher.

### 3.7. Implications for the HCHO source identification in Guangzhou

In our past studies, some atmospheric HCHO carbon isotope data were achieved. There was a bus station near the Guangzhou East Railway Station in Tianhe District, which corresponded to an area of ca. 17,300 m<sup>2</sup>, with a roof, 8 exits and 8 carriage drives. The bus station could raise the rate of 4500 bus day<sup>-1</sup>. It was not only a parking place, the buses came and went frequently and there were many passengers waiting for the buses (Feng et al., 2005). In such a closed environment, vehicle emission was the main source of atmospheric pollutants. It was the same for HCHO, which was proved by the accordance of carbon isotopic data of atmospheric HCHO (close to  $-20\text{‰}$ , Wen et al., 2005) and vehicle emitted HCHO (this study).

Also the atmospheric biogenic HCHO was collected in one of main mountaintops of Dinghushan Biosphere Reserve near Guangzhou, where the main HCHO sources were the biogenic emission and the secondary formation of the biogenic VOCs. The sample period was in winter and consumption of atmospheric HCHO was weak. The carbon isotopic data of directly biogenic emission and the atmospheric HCHO were in the range of  $-36$  to  $-46\text{‰}$ , and there were large deviations of carbon isotope data between these two types of HCHO, which indicated that the secondary formation was the main source of ambient HCHO in DHS-BR (detailed discussed in Guo et al., 2009).

The urban atmospheric HCHO was collected in the top of the building about 100 m away from a highway in Guangzhou in March, the HCHO carbon isotopic data were about  $-40\text{‰}$  (Yu et al., 2006). In such a sampling site, though the vehicle emission was supposed

to be one important source for the atmospheric HCHO, other sources like factory emission and secondary formation by atmospheric VOCs were also considerable. Meanwhile, when HCHO entered into atmosphere, complex consumption reactions, e.g. OH radical reaction and photolysis would occur to create inverse or normal isotope effect. The sources and the consumption processes would all affect the carbon isotopic data of atmospheric HCHO. For the limitation of carbon isotopic data, it was difficult to draw a reasonable conclusion on source identification of HCHO in urban air of Guangzhou, China.

## 4. Conclusions

In this study, the carbon isotopic composition and HCHO concentration in vehicle and stand-alone engine exhaust were analyzed. When compared with the carbon isotopic ratios of the fuel, the HCHO carbon isotopic ratios showed positive carbon isotopic fractionation, which might have resulted from the combination of production and consumption processes in the engine cylinder, particularly, from the consumption process, as noted in the engine test. With regard to the gasoline vehicles with catalytic converter, larger isotopic fractionation of HCHO was detected, indicating additional consumption process during catalysis. Furthermore, when compared with the HCHO emission factors reported in previous studies, those obtained in the present study were higher. Moreover, in a bus station in Guangzhou, South China, HCHO directly emitted from vehicle might be the major source of atmospheric HCHO. But for the limitation of isotopic data, it was hard to make it clear that the main sources of HCHO in the urban air of Guangzhou. But for the limitation of isotopic data, it was hard to make it clear that the main sources of HCHO in the urban air of Guangzhou.

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