



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‰ for gasoline engine, and from -26.2 to -20.7‰ 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‰). 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 (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 (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 NaHSO_3 were

employed to collect HCHO (Yu et al., 2006). For the measurement of 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 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 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 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[#] 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 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

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