

Research paper

An assessment of how bio-E10 will impact the vehicle-related ozone contamination in China

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ABSTRACT

Bio-E10 is short for the biofuel made up of 90% gasoline in volume and 10% bio-ethanol, which is the ethanol made from commercially-grown crops such as corn and wheat by the sugar fermentation process. In China, bio-E10 will be supplied nationwide from 2020 as an alternative to conventional gasoline, aiming at ensuring greater energy security and lowering the greenhouse gas emissions. In order to assess the impacts of the upcoming bio-E10 application on the ozone forming potential (OFP) of the emissions from in-use vehicles, this paper examined the carbonyls and volatile organic compounds (VOCs) in the evaporative and tailpipe emissions of three China-4 certified in-use vehicles fueled with a market-available gasoline and two match-blend bio-E10s, and calculated their OFPs using the Maximum Incremental Reactivity (MIR) method. The results revealed that for the evaporative emissions, the use of bio-E10s increased the carbonyl and VOC emissions released within the diurnal-loss stage by 8.5–17.6% and 11.1–78.6% respectively, but decreased the carbonyl and VOC emissions in the hot-soak stage by 47.4%–61.5% and 4.8%–20.6% respectively. Regarding the tailpipe emissions, in comparison to the gasoline baseline, burning bio-E10s increased the carbonyls by 15%–46% while reducing the VOCs by 37%–56% over the New European Driving Cycle (NEDC). Reductions in the tailpipe OFPs up to 47.3% were seen with the application of the bio-E10s, however, there were no clear conclusions with respect to the evaporative OFPs, which varied from –15% to +25% compared to the gasoline baseline. Based on the test results and census data, the application of bio-E10 in China is shown to help remove part of ozone contamination from the in-use vehicle sector.

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1. Introduction

Nowadays, many Chinese metropolitans are suffering from extreme weather induced by primary and secondary organic aerosols (SOAs) and ozone contaminations (Cheng et al., 2014), particularly in the areas with a high-density population like the Jing-Jin-Ji Area, Pearl River Delta and Yangtze River Delta (Huang et al., 2014; Sun et al., 2014). As reported, in China, the extreme weathers caused up to 1.1 million early morbidities and about 267 billion RMB loss annually (South China Morning Post, 2018). It has been confirmed that road vehicles played a significant role in the generation of SOAs and ground-level ozone (Huang et al., 2010). A previous study reported that the SOAs due to vehicle activities and coal-burning accounted for 45% to 65% of the annual particulate emissions in Beijing (Huang et al., 2014). Regarding ground-level ozone, it has been shown to increase early morbidity (Stedman, 2004) and was mainly formed via a

series of complicated photochemical reactions between nitrogen oxides (NO_x) and volatile organic compounds (VOCs) emissions, which are predominantly contributed by vehicle activities in urban regions.

In order to level the trade-off correlation between the ever-increasing global energy demand and the willingness to reduce greenhouse gas emissions, renewable energy has been widely implemented in many countries as a feasible solution (Demirbas, 2009; Wang et al., 2016b; Yang et al., 2012). Bio-ethanol, bio-methane and bio-diesel are the most successful examples implemented in the transport sector (Wang et al., 2017; Hu et al., 2006; Turner et al., 2013). Aiming at abating its national carbon dioxide (CO₂) emission and searching for a better way to consume the aged grains in-store, the central government of China announced a national program in 2017 encouraging the nationwide supply of bio-E10 from 2020 (National Energy Administration, 2017). Bio-ethanol is the ethanol produced from energy crops by the hydrolysis and sugar fermentation process helping offset CO₂ emissions oriented from vehicle operations. The most commonly-used biofuel in the transport sector is the blend containing 10% bio-ethanol and 90% gasoline, which is widely known as bio-E10

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('E' numbers describe the volumetric percentage of ethanol in the blend).

Switching from petroleum gasoline to bio-E10 will impact the tailpipe and evaporative emissions from in-use gasoline vehicles (Demirbas, 2009; Chin and Batterman, 2012; Franklin et al., 2001; Graham et al., 2008; Hulwan and Joshi, 2011), due to the changes in the fuel compositions, physicochemical properties, and related engine combustion characteristics. The use of bio-E10 may also cause some possible unfitness in current fleets since, in China, most of the in-use vehicles were developed and calibrated to burn gasoline only. Also, the charcoal canisters designed for gasoline may function improperly with bio-E10 given the theoretically higher vapor pressure of bio-E10. Both factors could turn into worsened in-use emissions, which will be unexpected and unacceptable. In light of these risks, it is essential to evaluate the impacts of the upcoming fuel-switching on the tailpipe and evaporative emissions from current fleets, especially some unregulated pollutants showing strong adverse health effects and tendencies to form ground-level ozone (Carter, 2010).

Many studies have examined the tailpipe emissions from gasoline and E10-fueled vehicles and engines in both new and in-use states. And the vast majority of them have shown that the addition of ethanol benefited the reduction of carbonaceous pollutants like carbon monoxide (CO), total hydrocarbons (THC) and particulate matter (PM) (Demirbas, 2009; Beer et al., 2011; Hochhauser and Schleyer, 2014; Wang et al., 2014; Iodice et al., 2016; Najafi et al., 2009; Costagliola et al., 2013; Cho et al., 2015), but the conclusions on NO_x emissions were not consistent (Aakko-Saksa et al., 2014; Karavalakis et al., 2014; Edwin Geo et al., 2019). This discordancy could mainly originate from the differences in (1) the fuel components and properties, (2) technical level of the test vehicles, and (3) operating conditions. Generally, in addition to the higher latent heat of E10, E10 with higher aromatic contents reduces the volatility of fuel therefore slightly worsening the in-cylinder combustion process and tends to lower NO_x (Anderson et al., 2014). However, the extra oxygen borne with ethanol could result in the use of lean mixtures, which increase NO_x emissions. Hence, fuel impacts upon early models seem to be more pronounced than recent ones equipped with more advanced after-treatment devices and smarter lambda control.

Regarding the unregulated species, Karavalakis et al. (2012) tested the unregulated emissions from two in-use vehicles according to the Federal Test Procedure (FTP) and found decreased formaldehyde and benzenes emissions but increased acetaldehyde with E10 compared to the gasoline baseline. Similar results were reported in some other researches (Beer et al., 2011; Jin et al., 2017; Pang et al., 2008; Pouloupoulos et al., 2001; Clairotte et al., 2013; Agarwal et al., 2015). Yu and Tao (2009) also indicated that the estimated life-cycle VOC emissions from E10-fueling vehicles were less than that from gasoline and more favorable for the control of ground-level ozone.

Suarez et al. (2015) tested the unregulated emissions from a Euro-5 certified flex-fuel vehicle and concluded that the severely worsened acetaldehyde and unburned ethanol emissions increased the ozone forming potential (OFP) of the tailpipe emissions tested with E10. Costagliola et al. (2016) drew an opposite conclusion that E10 helped reduce the tailpipe OFP of a Euro-3 compliant vehicle compared to gasoline fueling. Similarly, Wang et al. reported that shifting to E10 could decrease the tailpipe OFPs of a set of Euro-3 to Euro-5 in-use vehicles, but it was also noticed that the benefits of using oxygenated fuel became narrowed on the cars certified to more advanced emission standards (Wang et al., 2016a). Tibaquira et al. (2018) concluded an average reduction of 17% in the tailpipe OFPs with E20 replacing gasoline as well. George et al. (2015) measured the tailpipe VOC

emissions from three light-duty gasoline vehicles fueled with gasoline and E10 and calculated the corresponding tailpipe OFPs, but no statistical differences were found between the two fuels.

Hence, the impacts of burning bio-E10 to replace gasoline on the tailpipe OFP could vary from car to car and from fuel to fuel, no clear OFP tendencies have been established by far, and thus more research work is needed.

Compared to tailpipe emissions, less attention has been paid to the evaporative emissions from current in-use fleets and their related OFPs. However, according to Yamada, who detected more VOCs in the evaporative emissions than the tailpipe emissions (Yamada, 2013), the evaporative emissions may be a more pronounced ozone inducer. Particularly in China, the evaporative emissions from vehicles contribute about 40% of the annual VOC emissions of the country and the upcoming adoption of bio-E10 was shown to possibly further increase this share (Man et al., 2018). In theory, higher evaporative emissions with low-content ethanol-gasoline, such as bio-E10, are governed by the so-called "near-azeotrope" effect, which increases the Reid Vapor Pressure (RVP) of the blend to a level even greater than the RVPs of gasoline and ethanol, and strengthens the vaporization of the blended fuel (Dasilva et al., 2005; Dai et al., 2013). Hence, in addition to the tailpipe OFP, the OFP contributed by the evaporative emissions from in-use vehicles requires more care and assessment, in particular, some species in the evaporative emissions, like xylenes, were previously shown to have very high ozone-forming reactivity (Carter, 2010).

Schifter et al. (2011) found that the tailpipe emissions induced a higher level of ozone formation than the evaporative did base on the testing of a set of MY05-08 cars sold in Mexico. A limitation of this study is that only the hot-soak pollutants were measured instead of hot-soak plus diurnal-loss emissions as defined in the emission regulation. The so-called "hot-soak" and "diurnal-loss" emissions describe the evaporative HC emissions escaped from the fuel supply system after a certain period of vehicle driving and fuel vapor leakage due to the temperature change in fuel tank respectively. Apart from this, the conclusions agreed well with Graham et al. (2008), who tested one GDI and three non-GDI vehicles of the model year 1998 to 2003 and found comparably higher OFPs of the tailpipe emissions.

In part of the previous studies, only some key VOC species were measured and taken into account in the estimation of OFP (Seinfeld and Pandis, 2012; Na et al., 2003), however, the contributions of carbonyl emissions should not be overlooked since some carbonyls like formaldehyde and acetaldehyde also have very high ozone-forming reactivity (Carter, 2010, 1995). Ignoring the contribution of carbonyls will result in an underestimation of ozone formation, particularly for alcohol-containing fuels like E10, because theoretically carbonyl emissions are more easily created via fuel escape and alcohol oxidation.

Because of the limited knowledge about the impacts of the upcoming fuel switching to bio-E10 on the tailpipe and evaporative emissions from current fleets and their OFPs, this paper examined the carbonyl and VOC emissions from three China-4 (equivalent to Euro-4) compliant in-use vehicles burning market-available gasoline and two bio-E10 samples over the New European Driving Cycle (NEDC). Apart from China, the findings may also be referable for the U.S., EU, Brazil and other regions where a certain amount of ethanol is being blended into gasoline (Colon et al., 2001; Energy Independence and Security Act, 2007).

2. Experimental methods

2.1. Test vehicles and fuel

In order to assess how the upcoming nationwide switch from gasoline to bio-E10 will impact the ozone-inducive emissions

Table 1
Limit values for light-duty China-4 (gasoline, Type-I test only).

	CO	THC	NMHC	NO _x
Limits (g/km)	1.00	0.10	0.068	0.08

from in-use vehicles in China, in this paper, the tailpipe and evaporative emissions from three representative light-duty gasoline vehicles were tested according to the certification procedures of China-4 emission standard, which is equivalent to Euro-4 regulation. As of late 2017, about 47.5% of the in-use vehicles in China were China-4 certified, hence in this study, all the test vehicles were selected China-4 to create better representativeness for the in-use fleets in China. Based on the released annual sales statistics, test vehicle A and C were picked as representatives of the best-selling family cars (SUV and sedan), while vehicle B was the most widely used taxi model in the past five years ([China Association of Automobile Manufacturers, 2017](#)). All the test vehicles were acquired from the largest rental service in China with full maintenance history. All the three test vehicles were low on odometer when tested so that the artifacts due to engine and catalyst malfunctions could be minimized. For reference, the limit values of the China-4, which is equivalent to Euro-4, and the specifications of the three test vehicles are listed in [Tables 1 and 2](#) respectively.

Each test vehicle was tested with three fuels, namely a market-available gasoline as the base fuel and another two match-blend bio-E10s acquired from the same refinery. Fuel properties of the gasoline and both bio-E10 samples were compared in [Table 3](#). According to the reported created by the refinery, the two bio-E10 fuels shared the same gasoline base fuel feedstock, but to achieve a similar level of vapor pressure, high molecular-weight contents in bio-E10(B) were slightly increased since its comparably higher ethanol substitution ratio.

2.2. Test equipment and procedures

The tailpipe emissions were measured at chassis level over the NEDC by carefully following the certification procedures of the type-I and type-IV tests defined in China-4 (Euro-4). It should be clarified that although the NEDC has been replaced by the Worldwide Harmonized Light-duty Test Cycle (WLTC) for the type-approval of new vehicle models, it is still the only drive cycle in force for the verification of conformity of production (COP) and in-service conformity of pre-China-6 and pre-Euro-6 vehicles. Though the NEDC is widely criticized for its steady-state driving style, compared to the WLTC, its less aggressive acceleration, lower cycle-averaged speed and a maximum speed of 120 km/h could better represent the road conditions in China. Additionally, guaranteed by the mature certification procedures, sticking with the NEDC was helpful to promote the creditability of the test results and make them more comparable to the limit values and existing database.

Before testing, the test vehicles were placed in a climate chamber (IMTECH SFTF, Germany) for soaking for at least 12 h. The chassis dynamometer is a 48-inch roller, all-wheel drive, electrical chassis-dyno specifically designed for emission certification (MAHA ECDM-48L-4WD, Germany). The road resistances and inertias were set according to the reference mass of the test vehicles, which are shown in [Table 2](#). Regulated gaseous emissions were measured with a standard constant volume sampling system (HORIBA CVS-7400S, Japan) and a multi-component emission analyzer (HORIBA MEXA-7400LE, Japan). The unregulated emissions were sampled from the sampling bags after the finish of cycle driving and bag reading procedures using two sampling pumps (SKC AirCheck 2000, USA). Before each sampling, the flow

rates of the sampling pumps were calibrated using a soap-film flowmeter to assure accurate gauging. To promote the accuracy of unregulated emission measurement, a dilution air purification system (HORIBA DAR-3300, Japan) was also employed, which removed more than 99% of the hydrocarbons in the background and dilution gas and prevented overestimations.

The carbonyl emissions were sampled using pre-coated 2, 4-DNPH cartridges (SUPELCO LpDNPH-S10, USA) while the VOCs were sampled with metal sorbent tubes (AGILENT TENAX TA, USA). After the samplings, the qualification and quantification of the carbonyl and VOC substances were done with a high-performance liquid chromatography (AGILENT 1200 series, USA) and a gas chromatograph-mass spectrometer (AGILENT 6890N, USA) coupled with a thermal desorption (MARKES UNITY, UK) respectively. The sampling and analysis of the unregulated emissions were handled as regulated by the standard methods TO-11A and TO-18 established by the United States Environmental Protection Agency (EPA). In order to minimize the impact of sample loss, all the tubes were refrigerated after sampling and analyzed within three days. More details about the test facilities and procedures can be found in our previous study ([Li et al., 2015](#)).

In this paper, twelve carbonyls, namely formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, acrolein, acetone, methyl ethyl ketone, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, cyclohexanone, tolu aldehyde were reported with another eight VOC species, namely benzene, toluene, ethylbenzene, p-xylene, styrene, o-xylene, n-undecane and n-butyl acetate.

For each vehicle and fuel, the evaporative emissions were tested after the finish of its triplicated tailpipe emission tests. The tests of evaporative emissions were performed in a standard sealed house (IMTECH VT-SHED, Germany) following the procedures illustrated in [Fig. 1](#). As required by the regulation, the canister of the test vehicle was first emptied and then loaded with a mixture of 50% butane and 50% nitrogen to breakthrough before each test. Besides, the fuel tank of the test vehicle was refilled to 40% of its full capacity with the test fuel. In this paper, the evaporative emissions were the fuel vapor that escapes from the vehicle during the hot-soak and 24 h diurnal-loss tests. The sampling of the evaporative carbonyls and VOCs was carried out at the ends of hot-soak tests and diurnal-loss tests with the same pumps used in chassis-dyno tests. The storage and analysis of the evaporative samples were subject to the same procedures as the aforementioned tailpipe samples.

The fuel changes were done with care. The fuel tank of the test vehicle was drained as completely as possible and flushed with the new fuel twice. After flushing, the test vehicle was refilled with the new fuel and ran one NEDC and another Extra Urban Driving Cycle (EUDC) on the chassis-dyno for pre-conditioning purposes. EUDC is the fifth part of the NEDC, which is designed to reflect the rural and highway driving in Europe. This drive cycle lasts for 400 s and 4.052 km containing four constant speeds, namely 50, 70, 100, and 120 km/h. This high-speed driving procedure helped the engine control unit (ECU) of the test vehicle to finish self-learning and adapt to the new fuel, reducing artifacts.

2.3. Calculation of OFP

In this paper, the OFPs of the tailpipe and evaporative emissions were estimated using the Maximum Incremental Reactivity (MIR) method promoted by [Carter \(2010\)](#). The MIR values used in the calculations were those revised in 2010. The compounds considered in this research with their MIRs are listed in [Table 4](#). The calculation model of the MIR method is shown in Eq. (1).

$$\text{OFP} = \sum \text{MIR}_i \times E_i \quad (1)$$

where MIR_i and E_i are the MIR (gO_3/g) and distance-based emission factor (mg/km) tested on the chassis-dyno of compound i respectively.

Table 2
Specifications of the test vehicles.

Vehicle	Engine type	Transmission	Curb weight	Mileage
A	2.0L L4 114 kW, NA PFI, TWC	5-speed AT	1676 kg	3230 km
B	1.6L L4 82 kW, NA PFI, TWC	5-speed MT	1350 kg	2967 km
C	1.6L L4 89 kW, NA PFI, TWC	6-speed AT	1490 kg	14728 km

Table 3
Fuel properties of gasoline and bio-E10 samples.

	Method	E10(A)	E10(B)	Gasoline
Research octane number	GB/T 5487–2015	95.5	95.5	93.0
Motor octane number	GB/T 503–2016	83.5	83.3	82.5
Anti-knock index	Calculated	89.5	89.2	87.8
Density at 20 °C, g/cm ³	ASTM D4052–2015	0.754	0.755	0.744
Lower heating value, MJ/kg	Calculated	41.62	41.42	44.00
10% evaporated at, °C	GB/T 6536–2010	47.9	47.2	51.6
50% evaporated at, °C	GB/T 6536–2010	68.8	67.2	95.4
90% evaporated at, °C	GB/T 6536–2010	159.4	157.7	157.5
Final boiling point, °C	GB/T 6536–2010	187.7	187.9	187.2
Residue, %(v/v)	GB/T 6536–2010	1.0	1.0	1.0
Vapor pressure, kPa	ASTM D5191–12	73.6	73.6	63.0
Ethanol, %(v/v)	SH/T 0663–2014	9.92	10.77	<0.01
Benzene, %(v/v)	ASTM D6839–15	0.25	0.26	0.27
Paraffins, %(v/v)	ASTM D6839–15	43.8	43.6	44.6
Aromatics, %(v/v)	ASTM D6839–15	15.8	15.6	22.5
Naphthene, %(v/v)	ASTM D6839–15	6.6	6.5	7.0
Olefins, %(v/v)	ASTM D6839–15	24.6	24.2	25.8
Manganese, g/L	SH/T 0711–2002	0.011	0.011	0.0117
Iron, g/L	SH/T 0712–2002	<0.002	<0.002	<0.002
Lead, g/L	GB/T 8020–2015	<0.0025	<0.0025	<0.0025

Table 4
MIRs of the compounds considered in this paper (gO₃/g).

Carbonyls	MIR	VOCs	MIR
Formaldehyde	9.46	benzene	0.72
Acetaldehyde	6.54	toluene	4
Acrolein	7.45	n-butyl acetate	0.83
Acetone	0.36	ethyl benzene	3.04
Propionaldehyde	7.08	p-xylene	5.84
Crotonaldehyde	9.39	styrene	1.73
Methyl ethyl ketone	1.84	o-xylene	7.64
Methacrolein	6.01	n-undecane	0.61
Butanal	5.97		
Benzaldehyde	−0.67	carbon monoxide	0.056
Valeraldehyde	5.08		
Tolualdehyde	−0.59		
Cyclohexanone	1.35		

2.4. Uncertainty of obtained data

For each test vehicle and fuel, the standard deviation of the tailpipe emission results was calculated according to Eq. (2).

$$\text{standard deviation} = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (2)$$

where n denotes the test number (n = 3 in this paper), x_i is the result of the ith test, and \bar{x} is the average of repeated test results.

3. Results and discussions

3.1. Evaporative emissions

Figs. 2a and b illustrate the carbonyl and VOC emissions measured in the evaporative tests of the three vehicles. The shares belonging to each unregulated pollutant are also presented in the figures.

As shown in Fig. 2a, for all the vehicles, the total evaporative carbonyl emission from bio-E10(A) was always the highest among the three fuels, about 14% higher than that of bio-E10(B) and

gasoline, while the emission trends between the results using gasoline and bio-E10(B) varied from car to car but in general, the total amounts were quite similar. Average carbonyl emissions were 25.5, 29.2, and 26.0 mg/test with gasoline, bio-E10(A), and bio-E10(B) being the test fuel. The results indicated that in this research, the “near-azeotrope” effect between gasoline and low-content ethanol increased the evaporative carbonyl emissions but this impact was limited, this is possibly because (1) carbonyls are mainly formed during fuel combustion, and (2) the two bio-E10s tested were both match-blends, which means that an extra small part of heavy hydrocarbons had been added the fuel to reduce the RVP increase caused by azeotropic phenomenon. Apart from the total carbonyls, no significant differences in the leading OFP contributing species like formaldehyde (3.1, 4.3, and 3.4 mg/test for gasoline, bio-E10(A) and bio-E10(B)) and acetaldehyde (3.1, 4.5, 4.0 mg/test for gasoline, bio-E10(A) and bio-E10(B)) could be observed in Fig. 2a. Given the same vapor pressures of the two bio-E10 samples but higher ethanol substitution ratio of bio-E10(B), a possible reason for the relatively lower evaporative carbonyl emissions from bio-E10(B) is that a higher content level of evaporated ethanol, which had not been accounted into evaporative carbonyls in Fig. 2a, may present in the evaporative emissions and reduce the portions of other species.

Among the species identified in Fig. 2a, cyclohexanone was the single predominant carbonyl compound of the evaporative emissions from all the vehicles and fuels. About 40%–50% of the evaporative carbonyl emissions were identified as cyclohexanone. This conclusion was consistent across all the three test fuels. Cyclohexanone detected in the evaporative emissions is plausibly a product of the oxidation of cyclohexane, which is a constituent of gasoline. The oxidation reactions can happen at room temperature with sunlight being the catalyst (Du et al., 2004). Based on this hypothesized reason, it seems reasonable that the gasoline base and bio-E10s released similar levels of cyclohexanone since about 90% of the bio-E10s were still gasoline.

As shown in Fig. 2b, toluene dominated the total evaporative VOC emissions from all the test vehicles with mass ratios ranging from 46% to 68%, followed by (m-, o-, p-) xylenes (21%–24%) and ethylbenzene (8%–9%). Benzene only occupied relatively

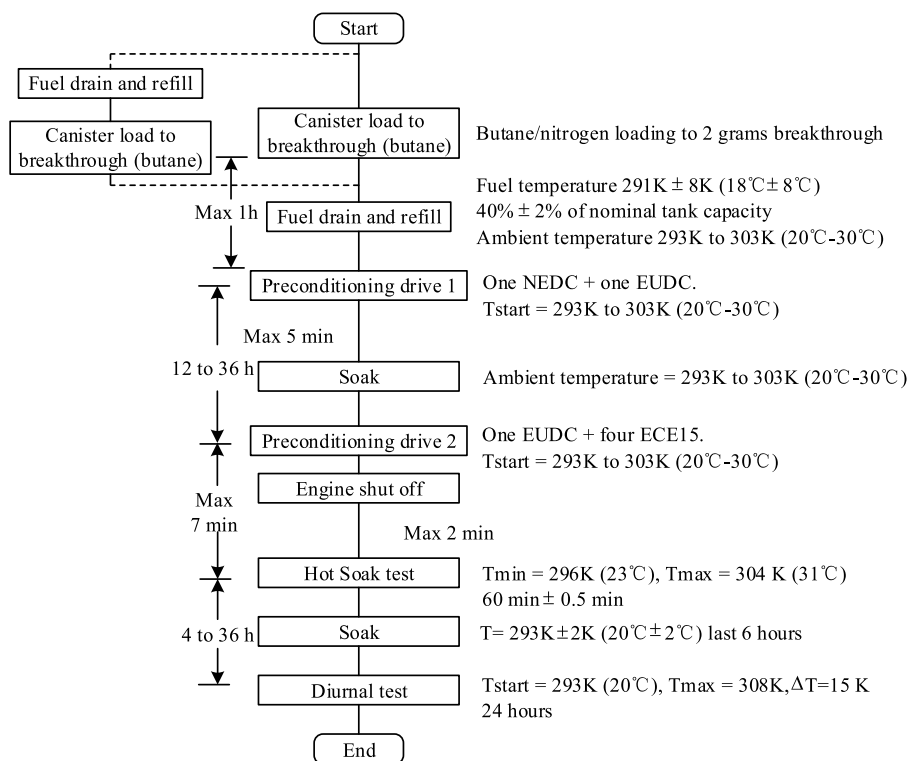


Fig. 1. Standard test procedures for the evaporative emissions in China-4.

small shares (less than 8%) in all the tests, primarily because its content has been strictly confined to below 1.0% in the fuel standard and the majority of the evaporative emissions should be fuel-borne species (Bailey and Meagher, 1986). Compared to gasoline, the evaporative VOC emissions with Bio-E10(A) fueling increased significantly. These increases ranged between 8% to 43% for individual species. This result accords well with previous studies concluding that “near-azeotrope” effect between gasoline and low-content ethanol elevated evaporative VOC emissions (Li et al., 2015). By contrast, a decrease in the evaporative VOC emissions from bio-E10(B) was noticed, this is plausibly due to the fact that the content of high molecular-weight hydrocarbons in bio-E10(B) was slightly raised, thus the tendency of the azeotropic phenomenon was weakened. Moreover, the addition of high molecular-weight contents diluted the concentrations of volatile compounds, underlining the evaporative VOC emissions as well. It should be mentioned that due to the very low concentrations of n-butylacetate and n-undecane identified in the tests (less than 1% of the total VOCs mass), the patterns representing these two species are too narrow to be seen in Fig. 2b.

As defined in the methodology section, the evaporative emissions illustrated in Fig. 2 are divided into hot-soak and diurnal-loss stages. The hot-soak emissions are mainly influenced by the fuel vapor remaining in the fuel delivery system while the diurnal-loss shows a closer correlation with the vapor escaped from the fuel tank. It can be seen in Tables 5 and 6 that for all the vehicles and fuels, the diurnal-loss is always to various degrees higher than the hot-soak emissions determined by its longer testing period. As compared in Table 5, the evaporative carbonyl emissions tested in the hot-soak stage with gasoline were always the highest among the three fuels for all the vehicles. On average, the hot-soak carbonyl emissions with gasoline fueling was 5% and 26% higher than those with bio-E10(A) and bio-E10(B), respectively. However, the evaporative carbonyl emissions of gasoline seen in the diurnal-loss stage were the lowest, the crew-average diurnal-loss carbonyl emissions with

gasoline fueling were 15% and 7% lower than those with bio-E10(A) and bio-E10(B). It can be seen at the bottom of Table 5 that the evaporative formaldehyde and acetaldehyde emissions with gasoline fueling were basically smaller than the two bio-E10s, indicating that the evaporative carbonyls from the gasoline base should be the chemicals with higher molecular weights oriented from the fuel compounds. Regarding the formaldehyde and acetaldehyde noticed with gasoline, they possibly came from the oxidation of Methyl tert-butyl ether (MTBE) or Ethyl tert-butyl ether (ETBE), which were commonly added in conventional gasoline as octane boosters.

Both bio-E10s yielded heavier diurnal-loss carbonyl emissions than gasoline. The leading reason for this phenomenon is the “near-azeotrope” effect, which raises the RVP of low-content alcohol-gasoline blends. Compared to gasoline, the RVPs of the two bio-E10s were approximately 10 kPa higher, underlying the more evaporative carbonyls seen within the diurnal-loss tests.

Table 6 divided the evaporative VOC emissions from the vehicles and fuels into two parts: hot-soak and diurnal-loss. It can be seen that the evaporative VOC emissions within the hot-soak stage measured with gasoline were still the highest, particularly benzene and toluene, since the VOC contents in the bio-E10s had been diluted by the addition of ethanol. In the diurnal-loss tests, the evaporative VOCs tested with gasoline fueling declined again and were generally the smallest among the three fuels. This is because, in comparison to hot-soak emissions, which are marginally impacted by temperature, the diurnal-loss emissions are more closely related to the distillation profile of fuel. Additionally, underlined by the “near-azeotrope” effect, some compounds in the bio-E10s became easier to evaporate and resulted in greater evaporative VOCs. The hot-soak VOC emissions of gasoline were 1.9 and 2.6 times those tested with bio-E10(A) and bio-E10(B), while the diurnal-loss VOC emissions of gasoline were 56% and 90% of the amount with bio-E10(A) and bio-E10(B) fueling.

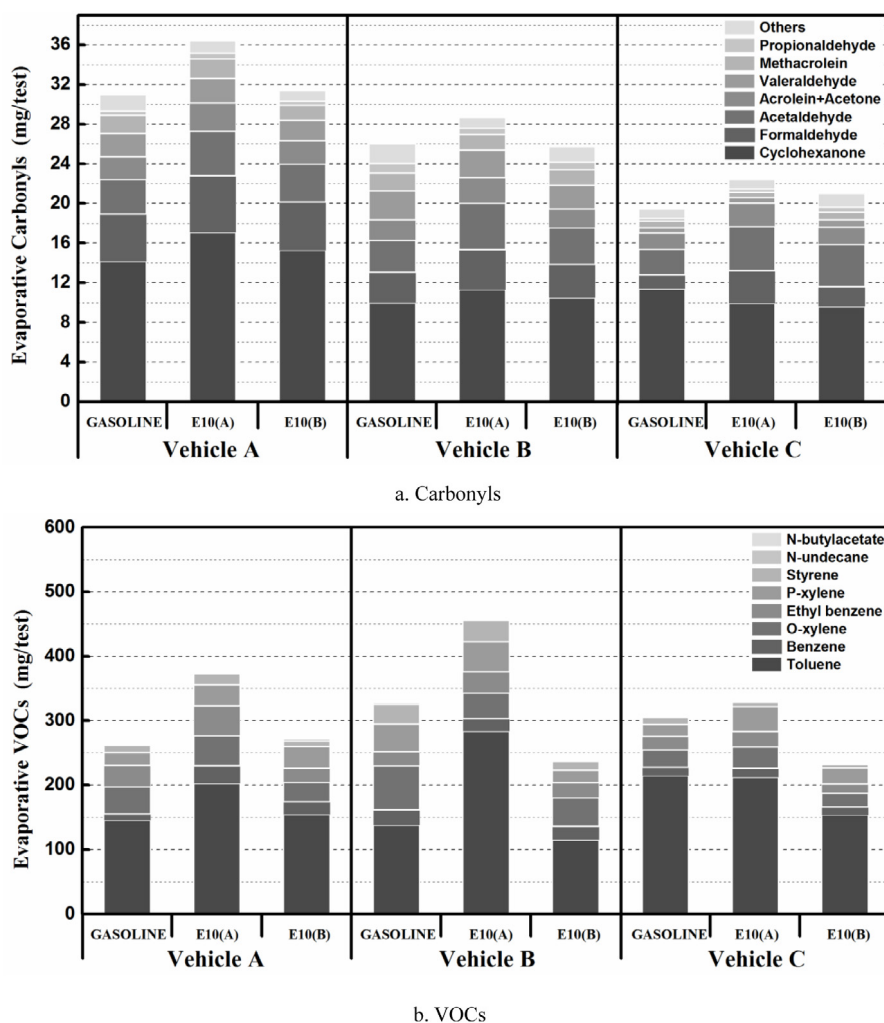


Fig. 2. Carbonyl and VOC emissions measured in the evaporative tests.

Table 5
Evaporative carbonyl emissions measured in hot-soak and diurnal-loss stages (mg/test).

Carbonyls	Hot-soak emissions			Diurnal-loss		
	Gasoline	E10(A)	E10(B)	Gasoline	E10(A)	E10(B)
Vehicle A	5.30	5.02	3.81	25.64	31.39	27.54
Vehicle B	4.24	4.01	3.25	21.77	24.64	22.45
Vehicle C	3.71	3.63	3.39	15.73	18.78	17.62
Formaldehyde (averaged)	0.93	1.41	1.04	2.18	2.93	2.38
Acetaldehyde (averaged)	0.32	0.48	0.22	2.77	4.06	3.72

3.2. Tailpipe emissions

Figs. 3a and b illustrate the tailpipe carbonyl and VOC emissions measured over the NEDC, the contribution of each unregulated pollutant is shown in the figures as well. Each vehicle and fuel were tested with 3 repeats, the error bars given in the figures were calculated based on the standard deviation of the results according to Eq. (2).

It can be seen in Fig. 3a that the total carbonyl compounds identified in the gasoline tests (0.73 ± 0.12 mg/km) were always lower than those emitted by the bio-E10(A) (0.84 ± 0.11 mg/km) and bio-E10(B) (1.07 ± 0.15 mg/km). The tailpipe carbonyl emissions from bio-E10(A) and bio-E10(B) increased by about 15% and

Table 6
Evaporative VOC emissions measured in hot-soak and diurnal-loss stages (mg/test).

VOCs	Hot-soak emissions			Diurnal-loss		
	Gasoline	E10(A)	E10(B)	Gasoline	E10(A)	E10(B)
Vehicle A	115.96	95.71	42.28	147.81	280.97	249.67
Vehicle B	151.49	89.00	78.25	176.65	366.96	161.03
Vehicle C	106.60	38.33	34.01	199.29	292.62	199.13
Benzene(average)	4.02	1.56	1.26	11.38	18.83	16.21
Toluene(average)	67.54	25.91	34.75	98.30	206.54	105.99

46% respectively, from the gasoline baseline. It is understandable that for all the three test vehicles, the tailpipe carbonyl emissions from bio-E10(B) were always 21%–33% higher than those from bio-E10(A) owing to the relatively higher ethanol content of bio-E10(B).

As shown in Fig. 3a, for all the test fuels, formaldehyde (30%) and acetaldehyde (45%) were the predominant carbonyl species in the tailpipe emissions. For the two bio-E10s, the portions of acetaldehyde (52%) were extremely high since acetaldehyde is a key intermediate governing the in-cylinder combustion and post-oxidation of ethanol (Poulopoulos et al., 2001). In general, the acetaldehyde emissions from the two bio-E10s were one to three times higher than the amount with gasoline on the same vehicle. Regarding the formaldehyde emissions, burning gasoline gave similar or slightly more formaldehyde than the bio-E10s

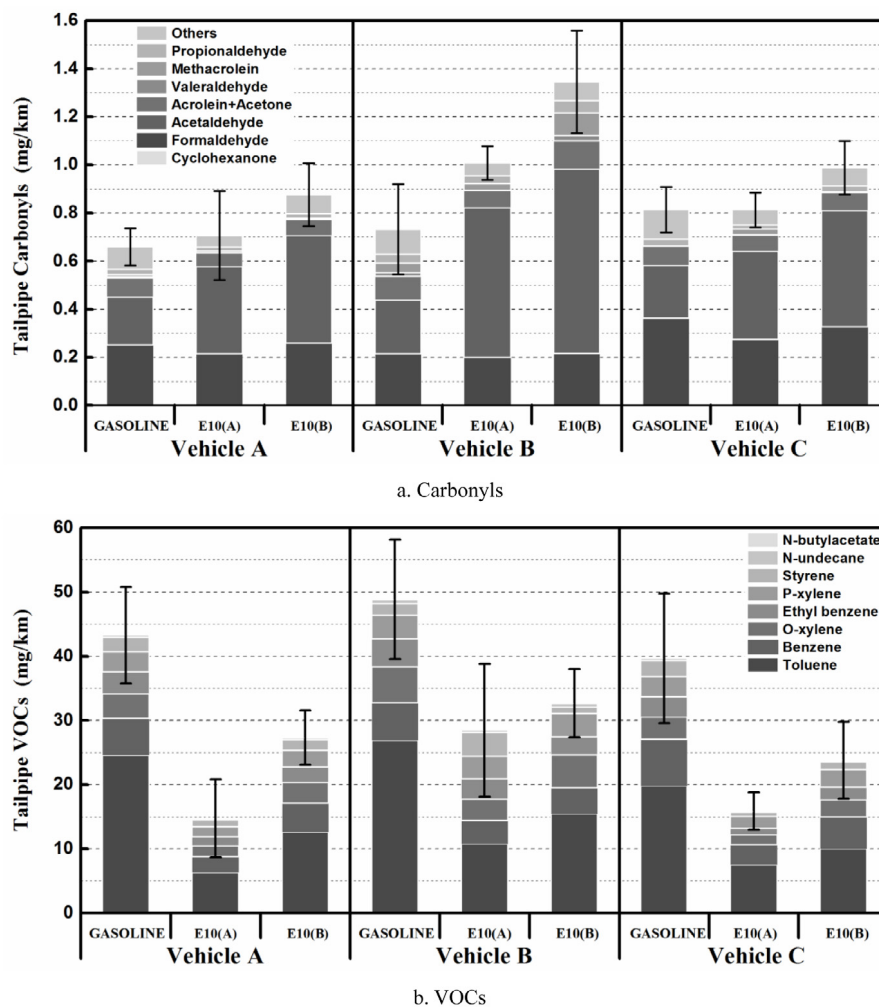


Fig. 3. Carbonyl and VOC emissions measured in the tailpipe tests.

for the addition of MTBE as an octane enhancer. Typically, MTBE or ETBE are unnecessary for bio-E10s since the octane number of ethanol has been high enough. Thus, the formaldehyde found in the exhaust emissions is considered a by-product of ethanol oxidation and gasoline flame quenching.

Against the carbonyls, the total tailpipe VOC emissions measured with gasoline (44 ± 9 mg/km) were always the highest among the three fuels tested. On average, the tailpipe VOCs identified with the bio-E10(A) (20 ± 6 mg/km) and bio-E10(B) (28 ± 5 mg/km) were 56% and 37% lower than those from gasoline. The blending of about 10% ethanol into gasoline diluted the content of aromatics in the bio-E10s, which could be a very important reason for the decreased tailpipe VOC emissions. Besides, there are only two carbon atoms in an ethanol molecule, it is quite hard to form any resultant with a ring structure. This factor might help further reduce the tailpipe VOC emissions from bio-E10 burning. In terms of the two bio-E10 fuels, the tailpipe VOC emissions from bio-E10(B) were consistently heavier relative to bio-E10(A) because the high molecular-weight contents had been added into bio-E10(B) were too long-chain and sooty to achieve complete and clean in-cylinder oxidation. Consequently, higher concentrations of volatile materials were found in the exhaust.

As shown in Fig. 3b, followed by benzene (16%), toluene (47%) was the leading VOC compound in the tailpipe emissions for all the fuels tested. This observation agrees well with previous researches (Graham et al., 2008; Pouloupoulos et al., 2001; Bailey and Meagher, 1986; Stump, 1997) and could be supported by the

Table 7

The OFPs of the evaporative and tailpipe emissions.

OFP	Evaporative (mgO ₃ /test)			Tailpipe (mgO ₃ /km)		
	Gasoline	E10(A)	E10(B)	Gasoline	E10(A)	E10(B)
Carbonyls	102.66	124.95	108.36	4.81	5.67	7.09
VOCs	1291.68	1619.76	1077.33	166.93	74.13	109.25
CO	–	–	–	36.18	29.87	31.88
Total	1394.34	1744.71	1185.69	207.92	109.67	148.22

studies conducted by Saxer et al. (2006), who concluded benzene as a by-product of the oxidation of toluene in three-way catalysts. Similar to the case in Fig. 2b, since the mass of n-butylacetate and n-undecane quantified in the absorbent tubes only occupied about 1.5% of the total tailpipe VOC emissions, in most of the cases, the patterns belong to these two species are very difficult to be observed in Fig. 3.

3.3. OFPs

Table 7 summarizes the crew-averaged tailpipe and evaporative OFPs of the three test fuels. In addition to the carbonyls and VOCs, the contribution of CO is also considered in the calculation of the OFPs.

It can be seen in Table 7 that the application of bio-E10s reduced the tailpipe OFPs by up to 47.3% from the gasoline

baseline, due to the markedly decreased VOCs and slightly dwindled CO emission. However, uncertainties are seen regarding the evaporative OFPs with a broad margin from -15% to $+25\%$.

On both the evaporative and tailpipe OFPs, the VOCs show much stronger impacts than the carbonyls in Table 7. Even the CO emissions were shown more influential than the carbonyls on the tailpipe OFPs. Even so, neglect of carbonyls could result in an up to 9% underestimation of the evaporative OFP in comparison to that with only VOCs being considered. An omission of CO would also underestimate the overall OFP by 17.4% to 27.2%.

Given the different units of the evaporative and tailpipe emissions, it is meaningless to make any straightforward comparison in between. It will be more practical to assess the impact of each emission by linking the OFPs provided in Table 7 to the scenarios in different areas.

In China, for example, according to a statistic conducted by the Vehicle Emission Control Center of China, an average passenger car ran 26910 km annually or 73.7 km/day (Du et al., 2004). In this case, the tailpipe emissions should dominate the OFP (90%) of vehicle emissions, then the application of bio-E10 will be helpful to a reduction of the ozone contamination induced by vehicle activities, decreased OFP by about 30%–40%. It is also understood that the national data might be too large for an assessment of some small cities since the commutes there can be much shorter and short commutes promotes the significance of evaporative emissions in the overall OFP. Nevertheless, according to Table 7, it can be calculated that the use of bio-E10 will see its OFP benefit if the commute is longer than 4 km per day, a distance much shorter than the majority of private mobilities. Consequently, the nationwide adoption of bio-E10 in 2020 will generally benefit a reduction in the vehicle-related ozone contamination in China.

Unlike new models, there is no forcible way to upgrade the technical status of the in-use vehicles to realize emissions reduction purposes, and it is more practical to achieve such goals via greening the national fuel supply like the upcoming bio-E10 case in China. Given that the benefits of switching from gasoline to bio-E10 are the reduction in tailpipe VOCs while the challenges are the increased evaporative emissions induced by ethanol addition, the goal of “cleaner fuel derives smaller pollution” could be only guaranteed by qualified fuels. Thus, the long-term implementation of stringent market fuel surveillance programs becomes essential and inevitable. Random inspection of fuel samples purchased from the market will be an effective tool for such policies. Ideally, all the indices of the fuel samples shall be tested to ensure that they always conform to the regulatory caps. However, it will be too expensive and time-consuming to carry out all the measurements, especially for on-site inspection. Among tens of indices, it is highly recommended to consider the checks of density, ethanol/vapor pressure, and aromatics contents with the highest priority.

(1) Density: both the density of ethanol and aromatics are heavier than gasoline, a quick check of sample density will be helpful to screen the fuel with an excessive addition of ethanol and/or aromatics out.

(2) Ethanol/vapor pressure: currently, the price of ethanol is much cheaper than gasoline in China, over-high ethanol addition secures larger profit but increases the vapor pressure and therefore evaporative emissions, accelerating the formation of SOA and ozone.

(3) Aromatics: high aromatics content in bio-E10 could usually be a result of the use of gasoline feedstock received insufficient catalytic cracking (to cut expense down) or artificially over addition to control vapor pressure within regulatory range. Despite these reasons, the consumption of high aromatics gasoline will cause a remarkable increase in the tailpipe VOC emissions that thrive ozone.

4. Conclusions

In order to assess the impacts of the upcoming bio-E10 application on the vehicle-related ozone contamination in China, the carbonyls and VOCs existing in the evaporative and tailpipe emissions from three China-4 certified in-use vehicles were tested with a market-available gasoline and two match-blend bio-E10s, and the OFPs of the unregulated emissions were calculated using the MIR method. The main conclusions are drawn below.

Evaporative emissions: the bio-E10s increased the carbonyl and VOC emissions identified within the diurnal-loss tests but decreased those found during the hot-soak stage. Cyclohexanone was found the leading carbonyl in the evaporative emissions from all the test fuels while toluene being the main VOC substance.

Tailpipe emissions: the bio-E10s generally increased the carbonyls emitted over the NEDC, but in comparison to the gasoline base, the VOCs became less. Acetaldehyde dominated the tailpipe emissions from both bio-E10s. With respect to the gasoline base, formaldehyde was equal to or slightly higher than acetaldehyde in the tailpipe emissions.

OFPs: the bio-E10s reduced the tailpipe OFPs from the gasoline baseline, but uncertainties were seen regarding the evaporative OFPs. An omission of carbonyls and CO in the calculation of OFP could result in an underestimation of up to 9% and 27.2% respectively. Based on the test results and the statistical data surveyed by a governmental department, the calculations of the evaporative and tailpipe OFPs indicated that in China, the upcoming application of bio-E10 would be beneficial to a reduction in the ozone contamination induced by vehicle activities.

Abbreviations

AT	Automatic Transmission
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
COP	Conformity of Production
ECU	Engine Control Unit
EPA	United States Environmental Protection Agency
ETBE	Ethyl Tert-butyl Ether
EUDC	Extra Urban Driving Cycle
FTP	Federal Test Procedure
HC	Hydrocarbons
MIR	Maximum Incremental Reactivity
MT	Manual Transmission
MTBE	Methyl Tert-butyl Ether
NA PFI	Naturally Aspirated Port Fuel Injection
NEDC	New European Driving Cycle
NMHC	Non-methane Hydrocarbons
NO _x	Nitrogen Oxides
OFP	Ozone Forming Potential
PM	Particulate Matter
RVP	Reid Vapor Pressure
SOAs	Secondary Organic Aerosols
THC	Total Hydrocarbons
TWC	Three-way Catalytic Converters
VOCs	Volatile Organic Compounds
WLTC	World Harmonized Light-duty Test Cycle

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Mengzhu Zhang: Writing - original draft, Formal analysis, Visualization, Investigation. **Yunshan Ge:** Conceptualization,

Methodology, Supervision. **Xin Wang:** Writing - review & editing, Conceptualization, Formal analysis, Investigation, Funding acquisition. **Daisy Thomas:** Writing - review & editing. **Sheng Su:** Methodology, Resources, Investigation. **Hu Li:** Writing - review & editing.

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