Carbonyl compounds from typical combustion sources: emission characteristics, influencing factors, and their contribution to ozone formation

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Abstract. Combustion sources are the important primary emission sources of carbonyl compounds (CCs), yet the emission factors (EFs) and influencing factors for CCs in different sources remain unclear. The emission characteristics, influencing factors, and ozone formation potentials (OFPs) of CCs from four combustion sources, including biomass burning (BB), residential coal combustion (RCC), on-road sources, and agricultural machinery (AM), were investigated by field measurements. Results indicate that the EF_{CCs} from four combustion sources exhibit significant differences. Specifically, the EFs from BB (1968.2±661.2 mg/kg) are significantly higher than other sources, being an order of magnitude greater than the on-road sources (117.8±78.3~576.3±47.4 mg/kg). Fuel types is key factors affecting the CCs components. BB primarily emit formaldehyde and acetaldehyde (F+A), accounting for 80% of CCs, whereas RCC exhibits a higher proportion of aromatic aldehydes and acetone (26.0%). The addition of ethanol in on-road sources and biodiesel in AM effectively promotes the formation of acetaldehyde (67.9%) and unsaturated aldehydes (20.4%), respectively. The formation of CCs in solid and liquid fuel sources is more sensitive to combustion temperature and emission standards, respectively. Higher combustion temperature and stricter emission standards can reduce CCs emissions by 94.6% in solid fuels and by 61.3% in liquid fuel, respectively. High-temperature promotes small molecules like F+A tend to cyclize, supplying ample precursors for the formation of acetone and aromatic aldehydes. More attention should be paid to the OFPs of CCs from BB and AM to allevite the oxidizing capacity of regional atmospheres.

1 Introduction

Carbonyl compounds (CCs) are important intermediates in atmospheric photochemical reactions and are also significant
35 precursors for ozone (O_3) (Zhang et al., 2019; Ling et al., 2020) and secondary organic aerosols (SOA) (Shen, 2013; Mellouki et al., 2015; Go et al., 2024). CCs play a crucial role in regulating the oxidizing capacity of the atmosphere and have profound effects on the environment (Duan et al., 2008; Yang et al., 2018) and human health (Krzyzanowski et al., 2008; Weisel et al., 2017). Previous studies have shown that primary emission sources in ambient air are significant contributors to CCs and significantly influence the oxidizing capacity and photochemical reaction rates of regional atmospheres (Yang et al., 2018,
40 2024; Zhao et al., 2024). Tang et al. (2019) measured gaseous CCs at the junction of the Beijing-Tianjin-Hebei region and found that the main sources of small molecule CCs include vehicle emissions, solvent use, residential coal combustion (RCC) and biomass burning (BB). Zhang et al. (2020) conducted a study on the emissions of volatile compounds in the North China Plain during winter and discovered that RCC, BB, vehicle emissions, and solvent use are the primary sources of CCs emissions, consistent with the findings of Xie et al. (2021). It is evident that vehicle emissions, BB, and RCC are typical primary emission
45 sources of CCs. Therefore, investigating the emissions of CCs from BB, RCC, and vehicle emissions holds significant potential for controlling atmospheric oxidizing capacity.

At present, many studies have reported on the emissions of CCs from residential solid fuel combustion (RSFC), which includes BB and RCC sources. The results indicate that the emissions of CCs are influenced by combustion conditions (temperature, oxygen concentration, stove type) and fuel characteristics (type, composition, moisture content (MC)). For instance, Cheng et
50 al. (2022) investigated the emission characteristics (e.g., emission factors, EFs; chemical composition) of CCs from BB using the tube-furnace and found that combustion conditions (temperature, oxygen concentration) and fuel characteristics (composition) significantly affect the EFs and composition of CCs. Peng et al. (2023) explored the emission characteristics of CCs from poplar with varying moisture content and discovered that altering the MC can effectively reduce the formation of CCs. Similarly, Liu et al. (2022) conducted experiments with 19 types of fuels and tube-furnaces at low and high temperatures,
55 finding that both fuel types and stove types influence the emission characteristics and composition of CCs. Furthermore, the V_{daf} (the volatile matter content on a dry and ash-free basis) significantly affects the emission of CCs during RCC. For example, Feng et al. (2010) found that the concentrations of CCs and VOCs increase and then decrease with the maturity of RCC. However, current research lacks a systematic analysis of the impact of the different V_{daf} of coal samples on the emission characteristics of CCs. There is an urgent need to reveal the influence of the V_{daf} on the emission characteristics of CCs from
60 RCC, as well as the effects of different fuel types and combustion systems on the emission characteristics of CCs from RSFC, and to assess their contributions to atmospheric oxidizing capacity.

Numerous researchers have employed various methods to determine the emission characteristics of carbonyl compounds (CCs) from on-road sources, such as chassis dynamometer tests (Nelson et al., 2008; Guo et al., 2011; Karavalakis et al., 2011), tunnel experiments (Ho et al., 2007; Hung-Lung et al., 2007; Wu et al., 2021), and portable emission measurement systems
65 (PEMS) (Yao et al., 2015; Cao et al., 2020; Wang et al., 2024). Studies have found that different emission standards, fuel

types, and vehicle speeds all influence the emission characteristics and composition of CCs in vehicle exhaust. For instance, Liu et al. (2024) conducted emission tests on 15 light-duty gasoline vehicles (LDGVs) using a chassis dynamometer and found that the continuous updating of emission standards can significantly reduce CCs emissions, and the use of ethanol-blended gasoline can decrease the emissions of volatile organic compounds. Song et al. (2010) measured CCs emissions from diesel

70   engines and found that both fuels typically exhibit higher CCs emissions at high speeds compared to low and medium speeds. Ethanol-gasoline is characterized by its high combustion efficiency, high octane rating, and renewable nature (Costagliola et al., 2013; Zaharin et al., 2018). So it has been widely used as a partial substitute for gasoline and has been promoted and applied. Therefore, with the updating of emission standards and the improvement of fuel types and quality in China, it is particularly necessary to re-evaluate the impact and mechanisms of different ES and fuel types (such as ethanol-gasoline) on

75   the emission characteristics of CCs from on-road sources.

Agricultural machinery (AM), as an important component of non-road mobile sources, plays a significant role in seasonal severe pollution events through its emissions of CCs. Studies have found that different emission standards and fuel types significantly affect the emissions of CCs from AM. For example, Cao et al. (2020) studied the impact of biodiesel on CCs emissions using PEMS and found that stricter emission standards can significantly reduce the emission factors of CCs, while

80   the use of biodiesel has different effects on CCs emissions from different vehicles. Yu et al. (2023) tested the emissions of CCs from 20 agricultural machines with different emission standards using PEMS and found that emission standards significantly influence CCs emissions. In recent years, the Chinese government has actively promoted the development of the biodiesel industry, including applications in vehicles and ships. Studies have found that the use of biodiesel significantly reduces emissions of conventional pollutants such as CO and PM (Singh et al., 2016; Lou et al., 2022), but its impact on CCs

85   emissions is still not entirely clear. Therefore, it is necessary to assess the impact of biodiesel on CCs emissions, as well as the effects of different blends of diesel on the emission characteristics of CCs, and further explore their contributions to atmospheric oxidizing capacity.

To effectively control the emissions of CCs, it is necessary not only to supplement and update data from various combustion sources but also to conduct more detailed studies on the influencing factors of CCs emissions from BB and RCC, on-road

90   sources, and non-road AM sources. In this study, the emission characteristics and the key influencing factors of CCs were explored based on real-world measurements from four typical combustion sources. For BB and RCC, experiments were carried out in the real-stove and tube-furnace simulation combustion experiments to investigate the effects of fuel types (particularly the V_{daf} of coal) and combustion temperature (500℃, 800℃)on CCs emissions; as for on-road source, the urban closed-loop road measurements for gasoline and diesel vehicles were conducted to explore the effects of fuel types (such as ethanol-

95   gasoline), driving speeds (low/medium/high speed), and emission standards (China V and China VI) on CCs emissions; and concerning the non-road AM sources, the effects of emission standards and fuel types (such as biodiesel) on CCs emissions were executed based on field vehicle measurements. Finally, the contributions of the four typical sources to atmospheric oxidizing capacity were estimated by the ozone formation potentials (OFPs). This study will help deepen our understanding

100   of CCs emissions from different combustion sources, provide the latest data for improving emission inventories, and offer a
scientific basis for future air quality simulations and pollution control strategies.

2 Materials and Methods

2.1 Tested fuels and vehicles

Twelve common fuels were selected, including three types of straw (rice straw, wheat straw, and corn straw, which are widely
cultivated in southern and northern China), three types of wood (pine, poplar, and willow, representing softwood and
105   hardwood), and six types of coal with the different V_{daf} (LL coal, GJ coal, DT coal, SH coal, NM coal, and PX coal) (Table
S1). These fuels are typically used for cooking, heating, or burning activities in rural areas of China. In laboratory conditions,
the same fuels (2g) were used as controls, with combustion temperatures set at 500℃ and 800℃ to simulate ordinary stoves
and high-efficiency energy-saving stoves commonly used in daily life. A total of 43 samples from actual stoves and 94 samples
from laboratory tube-furnace simulations were obtained for RSFC.

110   On urban closed-loop roads, the emission characteristics of CCs in the exhaust of gasoline vehicles (GV) and diesel vehicles
(DV) were tested, examining the effects of fuel types, vehicle speeds, and emission standards on their emissions. Passenger
and commercial vehicles meeting the China V and China VI emission standards (2-4 vehicles per category) were selected to
assess the emission characteristics of regular gasoline, regular diesel, and ethanol-blended gasoline (Ethanol gasoline vehicles,
E-GV) under different driving speeds, including low speed (30 km/h), medium speed (60-90 km/h), and high speed (120 km/h)
115   (Table S2). Field vehicle measurements were conducted on non-road agricultural machinery in farmlands, selecting tractors
and harvesters meeting the China II and China III emission standards as experimental machinery to evaluate the emission
characteristics of CCs in the exhaust of regular commercial diesel (B0) and diesel/biodiesel blended fuels (Table S3). The
biodiesel was produced from waste cooking oil and mixed with commercial fossil diesel to create two blended fuels with
different ratios (B5, B20). A total of 67 samples from on-road sources and 69 samples from agricultural machinery were
120   obtained for mobile source sampling.

2.2 Sample collection and analysis

Emissions from typical combustion sources, including flue gas or exhaust, were collected using a laboratory-made sampling
dilution system, which comprises a dilution system and a sampling system. The detailed description of laboratory-made
sampling dilution system was presented in previous studies(Cheng et al., 2022; Liu et al., 2022; Peng et al., 2023). Briefly, the
125   clean air was introduced into dilution system via a fan, where it is mixed with the flue gas to achieve the purpose of diluting
the flue gas. And the concentration of CO_2 and CO in the flue gas was monitored in real-time using a flue gas analyzer (Photon-
II, Madur, Italy) to control the dilution ratio of the flue gas. The collection of CCs from the flue gas was accomplished using
an automatic CCs sampler equipped with 2, 4-dinitrophenylhydrazine (DNPH) coated cartridges. CCs can react with DNPH
to form stable hydrazone derivatives(Tang et al., 2003). The sampling flow rate was 0.5 L/min and DNPH cartridges were

placed behind quartz filters to collect gaseous CCs. After collection, the samples were immediately refrigerated at -4°C until analysis. The DNPH sampling tubes were placed in a vacuum glove box, and 2-3 mL of acetonitrile was used to elute the target compounds, which were then transferred to vials. The samples were quantitatively analyzed using high-performance liquid chromatography (HPLC) (1260; Agilent, USA) equipped with a UV detector and an Agilent TM C18 reverse-phase chromatographic column (5.0 μm, 250 mm × 4.6 mm). The mobile phase consisted of a mixture of water, acetonitrile, and tetrahydrofuran in a specific ratio to ensure optimal separation efficiency. A total of 20 CCs were analyzed, including formaldehyde (FA), acetaldehyde (ALD), acetone (ACE), unsaturated aldehydes (UA) (acrolein, crotonaldehyde), aromatic aldehydes (AA) (benzaldehyde, m/p-methylbenzaldehyde, o-methylbenzaldehyde, dimethylbenzaldehyde), and other aldehydes and ketones(OA) (propanal, butaldehyde, cyclohexanone, isopentanal, pentanal, heptanal, octanal, nonanal, decanal). QA/QC details are provided in the supplementary materials.

2.3 Calculation of the emission factors

In this study, the emission factors (EFs) of target compounds, based on the carbon balance, were calculated by Eq. (1)-(6)(Qian et al., 2021; Liu et al., 2022; Zhang et al., 2024). It is assumed that during combustion, all carbon in the fuel (excluding carbon in the ash) is primarily converted into CO, CO_2, and particulate carbon (OC, EC), i.e.:

$$m_{c-fuel} - m_{c-ash} = m_{c-CO_2} + m_{c-CO} + m_{c-OC} + m_{c-EC} \tag{1}$$

Incomplete combustion factor:

$$K = \frac{m_{c-CO} + m_{c-OC} + m_{c-EC}}{m_{CO_2}} \tag{2}$$

EFs of carbon in the form of CO_2:

$$EF_{CO_2} = \frac{m_{c-fuel} - m_{c-ash}}{(1+K)M} \tag{3}$$

When the mass of carbon in the ash is significantly lower than the mass of carbon in the fuel:

$$m_{c-fuel} - m_{c-ash} = Mk_{c-fuel} \tag{4}$$

where, m_{c-fuel} and m_{c-ash} represent the carbon mass in the fuel and ash, respectively. m_{c-CO_2} and m_{c-CO} denote the carbon mass in CO_2 and CO, respectively. m_{c-OC} and m_{c-EC} are the masses of organic carbon and elemental carbon in particulate matter, respectively. M is the mass of residential solid fuel (kg), and k_{c-fuel} is the carbon content of the residential solid fuel determined by elemental analysis.

$$EF_{CO_2} = EF_{C-CO_2}f_{CO_2} = \frac{(m_{c-fuel} - m_{c-ash})f_{CO_2}}{(1+K)M} = \frac{k_{c-fuel}f_{CO_2}}{(1+K)} \tag{5}$$

$$EF_i = \frac{C_i}{C_{CO_2}} EF_{CO_2} \tag{6}$$

where f_{CO_2} is the conversion factor, taken as 3.67. C_i and C_{CO_2} are the mass concentrations of target compound i and CO_2, respectively (μg/L), and EF_{CO_2} is the emission factor of CO_2.

2.4 Oxidizing capacity assessment calculation

160 The ozone formation potentials (OFPs) of CCs can be predicted based on the maximum incremental reactivity (MIR) values of specific species, and the specific Eq. (7) is as follows(Yu et al., 2023; Zhang et al., 2024).

$$OFP=\Sigma(MIR_i \times EF_i) \tag{7}$$

where OFP$_i$ is the ozone formation potential of a specific species i in CCs (g O$_3$)/(kg-fuel); MIR$_i$ is the maximum incremental reactivity of species i (Table S4) (Zhang et al., 2021), and EF$_i$ is the emission factor of CCs species i (g/(kg-fuel).

165 **3 Results and discussion**

3.1 Emission characteristics and influencing factors of CCs from RSFC

For real stoves, the EFs of CCs from BB (1676.4±989.5 mg/kg) are found to be significantly higher than that from RCC (287.9±79.2 mg/kg) (t-test, $p > 0.05$) (Table 1). The difference is attributed to the high emission of CCs being closely related to the high oxygen content of the fuel, such as the oxygen content of biomass (44.0±11.5%) being much higher than that of

170 residential coal (~10%). Table 1 presents the EFs of 20 CCs emitted from the combustion of two types of biomass (straw and wood) and residential coal. The EFs of CCs from BB and RCC are 1676.3±989.5 mg/kg and 287.9±79.2 mg/kg, respectively. The EFs of CCs from BB is approximately eight times that of RCC. Among these, the EFs of CCs from straw combustion (SC) (2384.1±1515.0 mg/kg) is about 2.5 times that of wood combustion (WC) (968.6±464.0 mg/kg), which may be attributed to differences in fuel structure and MC(Cheng et al., 2022; Peng et al., 2023).

175 The composition of CCs is significantly influenced by fuel types. Formaldehyde and acetaldehyde are the most abundant CCs in all three types of fuel, accounting for 71.3% (SC), 74.8% (WC), and 67.0% (RC) of the total CCs. Although the EFs of CCs from BB is much higher than that from RCC, the proportion of acetone in CCs emitted from RCC is higher than that from BB, representing 10.3% of the total CCs, while SC and WC account for 5.8% and 6.9%, respectively. There are significant differences in the proportion of unsaturated aldehydes among different fuels, with the proportion in SC being 1.7 times that of

180 WC and 2.9 times that of RCC. For aromatic aldehydes, the proportion in RCC is the highest (10.6%), while SC and WC account for 2.9% and 4.4%, respectively. The reason for this phenomenon is that the chemical structure of residential coal contains a higher content of aromatic compounds than biomass, which decompose during combustion, providing a large number of precursors for the formation of aromatic aldehydes. Additionally, the large error bars in each type of fuel indicate variability in emissions within the fuel, which may be related to combustion conditions. Therefore, this study conducted

185 simulation experiments in the tube-furnace to further explore the key influencing factors of CCs emissions of RSFC.

Table 1 EFs(mg/kg)of CCs in real stoves from RSFC

mg/kg	Straw	Wood	Coal
FA	1006.8±608.7	557.9±264.0	160.1±54.1
ALD	714.1±507.3	173.0±99.3	44.8±17.5
ACE	138.8±122.2	51.0±26.3	25.8±9.3
UA	273.5±210.4	64.6±34.1	11.4±5.3
AA	69.6±47.0	50.8±36.0	22.9±13.5
OA	245.7±164.9	63.7±30.7	22.7±9.0
ΣCCs	2384.1± 1515.0	968.6±464.0	287.9±79.2

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It should be mentioned that temperature is a key factor influencing the formation of CCs from RSFC. Fig. 1a, 1c show that the EFs of CCs from BB (straw and wood) and RCC under different influencing factors (temperature, O_2 concentration, MC, and V_{daf}). High temperatures significantly reduce the formation of CCs from RSFC, with reductions of 92.3%, 96.8%, and 51.1% for straw, wood, and residential coal, respectively. The reduction effect of high temperatures on CCs from BB is particularly

195 pronounced. Compared to temperature, MC also has a certain impact on the formation of CCs during BB. For instance, when the V_{daf} of fuels is close to 10%, the EFs of CCs is the lowest (832.0±160.2 mg/kg). As the MC increases, the EFs of CCs gradually rises, reaching a peak (2008.7±397.1 mg/kg) when the MC approaches 30%, which is about 2.4 times the minimum value (Peng et al., 2023). Therefore, selecting the optimal MC (10%) can achieve a maximum reduction effect of 58.6%. Similarly, the increase in O_2 concentration significantly reduces the formation of CCs. At the O_2 concentration of 21%, the

200 EFs of CCs for straw and wood are 4613.0 mg/kg and 6545.6 mg/kg, respectively. Compared to the O_2 concentration of 10.5%, the average EFs of CCs for SC and WC decreased by 33.2% and 36.8%, respectively. Furthermore, the V_{daf} also affects the emission of CCs from RCC. As the V_{daf} increases, the EFs of CCs first decreases (212.1±99.2 mg/kg) and then reaches a maximum value (372.9±53.7 mg/kg) when the V_{daf} is around 30%. According to the bell-shaped distribution theory by Chen et al. (2009), coal samples around 30% have special chemical characteristics, and these samples produce a large amount of

205 coal tar during combustion, which further increases the formation of CCs (Du and Li et al., 2022). In contrast, for coal types with the V_{daf} between 20% and 30%, the EFs of CCs decreases by 43.1%. Therefore, increasing combustion temperature, increasing O_2 concentration, selecting biomass fuels with the V_{daf} of 10%, or choosing coal samples with medium to low V_{daf} (around 26%) can effectively reduce the formation of CCs.

Different CCs species exhibit varying sensitivities to combustion temperature. Specifically, for BB and RCC, high

210 temperatures facilitate the degradation of formaldehyde and acetaldehyde while promoting the formation of acetone and aromatic aldehydes. As shown in Fig 1b, 1d, the EFs of formaldehyde, acetaldehyde, and acetone are significantly higher than those of other CCs, accounting for about 62.8% of the total CCs. This is consistent with the results of Schauer et al. (2001) and Liu et al.(2022). With the increase of combustion temperature, the proportions of formaldehyde and acetaldehyde in straw,

wood, and residential coal decreased by 34.6%, 37.7%, and 30.7%, respectively. In contrast, at higher temperature, the
215 proportions of acetone and aromatic aldehydes in the three types of RSFC increased by 19.8%, 19.6%, and 7.2%, respectively,
compared to those at lower temperature. It should be mentioned that small molecules, including formaldehyde and
acetaldehyde, are more sensitive to combustion temperature compared to larger molecules, due to their tendency to polymerize
or cyclize under high-temperature conditions (Peng et al., 2023). The mechanisms of acetone and aromatic aldehyde formation
in the flue gas from BB and RCC at high temperatures are significantly different. For BB, the formation of acetone and aromatic
220 aldehydes is closely related to the pyrolysis of lignin (Cheng et al., 2022). For example, high temperatures promote the
dehydration and isomerization of 1,2-propanediol, generated from the cleavage of alcoholic hydroxyl groups of lignin, to form
acetone (Caballero et al., 1997). Similarly, high temperatures facilitate the formation of aromatic aldehydes such as
benzaldehyde from the cleavage of aromatic ring side chains of lignin (Wang et al., 2017). In contrast to BB, the increase in
the proportion of acetone and aromatic aldehydes in RCC is attributed to secondary gas-phase reactions at high temperatures.
225 The conjugated bonds in the aromatic ring structure of coal break at high temperatures, providing more precursors for the
formation of acetone (Miura, 2000). At high temperatures, aromatic hydrocarbons generated from coal combustion undergo
secondary reactions and oxidation to form aromatic aldehydes such as benzaldehyde (Wang et al., 2017). The pattern of
aromatic hydrocarbons were reported by Qian et al. at high temperatures further verifies this mechanism (Qian et al., 2021).
Unsaturated aldehydes are insensitive to temperature changes, with their proportions fluctuating between 4.3% and 6.5% in
230 the three types of RSFC.
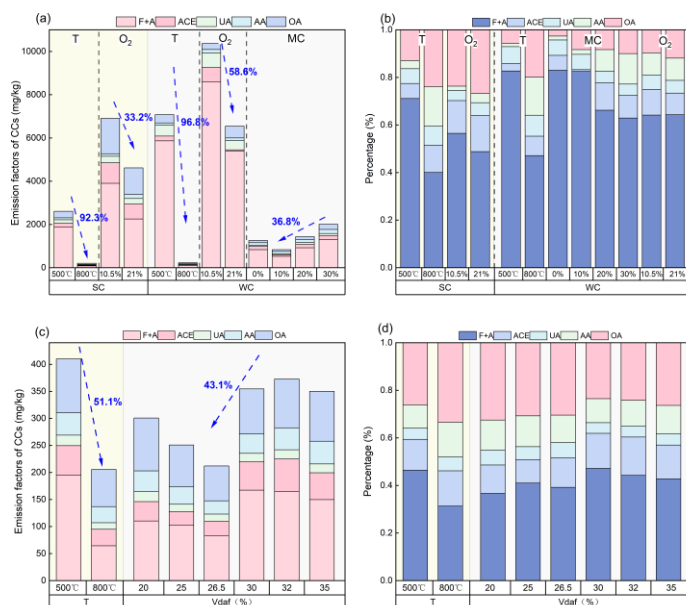
Figure 1: Differences in CCs emission characteristics and composition of RSFC under different influencing factors; T, Temperature; O₂, Oxygen concentration; F+A, Formaldehyde+ Acetaldehyde.

3.2 Emission Characteristics and Influencing Factors of CCs from On-road Sources

The formation of CCs from on-road vehicles is significantly influenced by fuel types and emission standards. As shown in Fig. 2a, 2b, the EFs of CCs exhibit that DVs emit more CCs than GVs, with the EFs of 214.1 ± 34.1 mg/kg for DV and 117.8 ± 78.3 mg/kg for GV. This result has also been frequently observed in previous findings (Ban-Weiss et al., 2008; Martinet et al., 2017; Wang et al., 2024), indicating that fuel types is a critical factor in the formation of CCs from on-road sources, achieving the 45.0% reduction effect. The higher emissions from diesel vehicles may be related to their combustion process, where excess air is present in the combustion chamber (i.e., the overall fuel-lean condition), leading to higher oxygen content and more oxidation processes during combustion (Pang et al., 2008; Gentner et al., 2017). Additionally, the use of ethanol-blended gasoline has a significant reduction effect on formaldehyde emissions, but the EFs of acetaldehyde in the exhaust significantly increases, changing the ratio of formaldehyde to acetaldehyde from 5.6:1 to 1:1. The EFs of acetaldehyde in ethanol-blended gasoline is 2.8 times that of gasoline (Magnusson et al., 2002). When 10% ethanol is added, the change in ethanol content has a minimal impact on the total emissions of CCs. This phenomenon is consistent with existing research findings, such as those by Karavalakis et al. (2014, 2015)and Yang et al. (2019), who also found that the use of ethanol-blended gasoline significantly affects the formation of acetaldehyde, while having a minor impact on total CCs emissions. Similarly, when emission standards are tightened, the average EFS of CCs for DV and GV decrease by 61.3% and 23.9%, respectively, indicating that stricter emission standards have a more significant reduction effect on DV emissions. This also suggests that the impact of emission standards on CCs emissions from GV is much lower than that on diesel vehicles. Vehicle speed is equally important for CCs formation. Data analysis reveals that for GV, DV, and E-GV, the distribution of CCs follows the pattern of low speed > high speed > medium speed (Figure 2). That is, at medium speeds (60~90 km/h), CCs emissions reach their minimum value (71.2 ± 21.1 mg/kg to 177.9 ± 22.8 mg/kg), with a maximum reduction of 55.9% in CCs emissions. This conclusion is consistent with the findings of Liu et al.(2024), and the likely reason is that combustion efficiency is highest at medium speeds, effectively reducing the formation of CCs. This phenomenon indicates that the impact of vehicle speed on emissions is nonlinear, and an optimal driving speed can enhance combustion efficiency, thereby effectively reducing CCs emissions.

Additionally, the types and composition of CCs were directly determined by fuel types (Figure 2c, 2d). GVs primarily emit small molecule CCs, such as formaldehyde, acetaldehyde, and acetone, accounting for about 78.9% of total CCs. In contrast, DVs emit more large-molecule aldehyde and ketone compounds, such as aromatic aldehydes (46.1%)(Gentner et al., 2012; Erickson et al., 2014; Yue et al., 2015), highlighting the importance of reducing emissions of heavier aromatic aldehyde CCs in DVs. This difference mainly stems from the compositional differences in the fuels. For example, diesel contains a higher proportion of medium to high carbon hydrocarbons (C_9-C_{23}), especially polycyclic aromatic hydrocarbons, which are more likely to oxidize to form aromatic aldehyde compounds. Gasoline, on the other hand, primarily consists of lower carbon straight-chain alkanes (C_4-C_{12}) and cycloalkanes (Gentner et al., 2017; Sorokina et al., 2021), resulting in the formation of more small molecule CCs. An inverse trend was observed for the effects of emission standards on the composition of CCs

from different fuel types. For instance, when emission standards are tightened, the proportions of formaldehyde and acetaldehyde decrease for both GV and DV, while the proportions of acetone and aromatic aldehydes show the opposite trend. The real reason for the difference in result was mainly attributed to the different exhaust treatment devices in the two types of vehicles, leading to varying removal efficiencies for the same pollutants (Russell and Epling, 2011). The impact of vehicle speed on the composition of CCs is not significant.
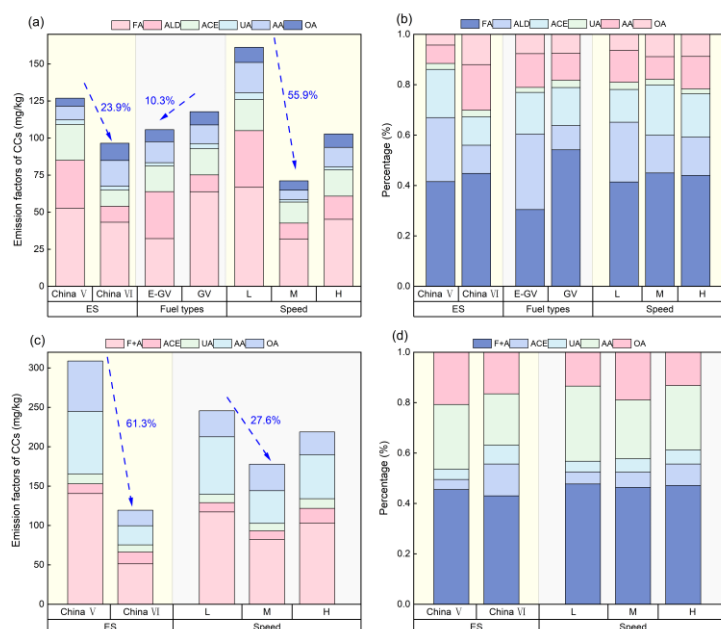
Figure 2: Differences in CCs emission characteristics and composition of gasoline vehicles(a、c)and diesel vehicles(b、d); E-GV, Ethanol-gasoline vehicles; ES, Emission standards; L, Low speed; M, Medium speed; H, High speed; FA, Formaldehyde; ALD, Acetaldehyde.

3.3 Emission characteristics and influencing factors of CCs from non-road sources

In the emissions of CCs from agricultural machinery, emission standards are considered as a key factor influencing emission characteristics. Figure 3a illustrate the EFs and composition of CCs from AM under different emission standards and fuel types. Similar to on-road vehicles, emission standards significantly affect the formation of CCs from AM. Specifically, the EFs of CCs from China III standard AM is significantly reduced compared to that from China II standard machinery (by 57.0%). This result indicates that raising emission standards can significantly decrease the formation of CCs from AM, especially for older China II standard machinery, where upgrading emission standards offers substantial potential for emission reduction. Additionally, the study found that the emission factor of CCs increased from 576.3 mg/kg for B0 to 785.9 mg/kg for B20, representing a 26.7% increase in CCs emissions (Figure 3). This trend is consistent with the conclusions drawn by

Karavalakis et al. (2011) and Prokopowicz et al. (2015) in existing literature, who suggested that the ester-based oxygen structure of biodiesel may be a significant factor contributing to the increase in CCs emissions. The higher oxygen content in biodiesel facilitates the formation of more carbon oxides during combustion, thereby increasing CCs emissions. Moreover, biodiesel may also affect the calorific value and density of the blended fuel, leading to decreased combustion efficiency (Guo et al., 2023), which further promotes the formation of CCs. With the increase in the proportion of biodiesel blending, some specific species in CCs change significantly. For example, the EFs of acrolein in B20 increased by 40.7% compared to B0, attributed to the oxidation of residual glycerol, saturated fatty acids, and unsaturated fatty acids in biodiesel (Graboski and McCormick, 1998). In contrast, since biodiesel does not contain aromatic hydrocarbons, the addition of 20% biodiesel reduced the EFs of aromatic aldehydes by 21.5% (Karavalakis et al., 2011). Additionally, the EFs of CCs from AM using diesel (576.3±47.4 mg/kg) is 2.7 times that of on-road DVs (214.1±85.3 mg/kg). The likely reason for this phenomenon is that emission standards (exhaust treatment technologies) for on-road diesel vehicles can reduce the CCs emissions of diesel (Sharp et al., 2000; Russell and Epling, 2011; Wang et al., 2022). The importance of updating emission standards for both on-road and non-road sources of CCs emissions was reaffirmed. In summary, although increasing the proportion of biodiesel blending can reduce emissions of some conventional pollutants such as CO and PM, it may also have adverse effects on CCs emissions, necessitating a comprehensive consideration of its emission reduction benefits and potential increases in emissions.
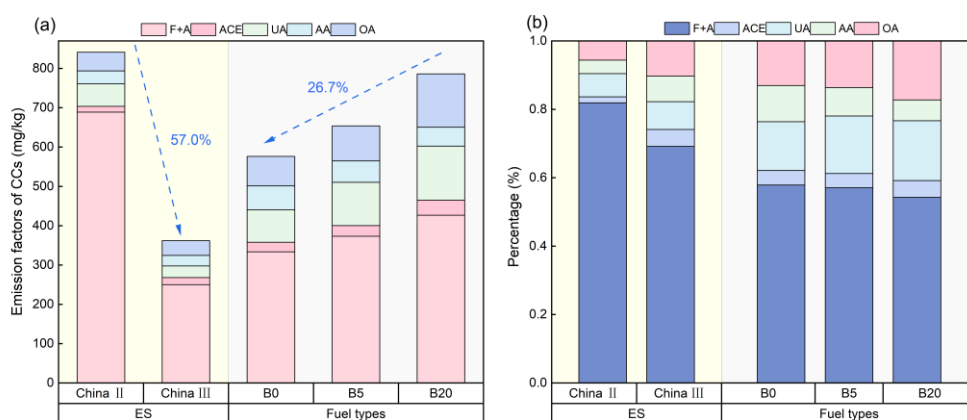
Figure 3: Differences in CCs emission characteristics(a)and composition(b)of non-road agricultural machinery

Upon analyzing the composition of CCs, it is observed that formaldehyde, acetaldehyde, and acrolein are the most abundant species in the emissions of CCs from agricultural machinery(He et al., 2009), accounting for 71.8% to 73.9% of the total emissions. (Figure 3b) However, as the proportion of biodiesel blending increases, the proportion of formaldehyde and acetaldehyde decreased by 6.2%, while the combined proportion of heavier compounds such as acetone, unsaturated aldehydes, and other aldehyde and ketone substances increased by 20.0%, which corresponds exactly to the 20% addition ratio of biodiesel

310   (v/v), indicating that the additional heavier CCs are entirely derived from the newly added biodiesel. Biodiesel, primarily composed of long-chain esters, is more likely to generate larger aldehyde and ketone compounds upon pyrolysis. The proportion of aromatic aldehydes is found to slightly decreased (by 4.5%) with the increase in biodiesel ratio, possibly because the addition of biodiesel reduces the content of aromatic hydrocarbons in the fuel, which are precursors for the formation of aromatic aldehydes. Overall, the blending of biodiesel significantly affects the composition of CCs, particularly by increasing

315   the generation of heavier aldehyde and ketone compounds while reducing the emissions of small molecules such as formaldehyde and acetaldehyde.

3.4 Emission Characteristics and Oxidative Potential Assessment of CCs from Different Combustion Sources

3.4.1 Emission Characteristics and Composition Comparison of CCs from Different Combustion Source

Significant differences are observed in the composition of CCs between RSFC (biomass, residential coal) and mobile sources

320   (on-road and non-road vehicles). Combustion temperature is a key factor affecting the formation of small molecule CCs, including formaldehyde and acetaldehyde. As depicted in Fig. 4, the proportion of formaldehyde and acetaldehyde in RSFC (69.2%) is typically higher than that in mobile sources (57.1%), which can be attributed to differences in combustion temperature. The combustion temperature of RSFCs (such as straw, wood, and residential coal), typically ranges lower (500-800°C), in contrast to the higher temperatures (1800-2000°C) of mobile sources. Under high-temperature conditions,

325   formaldehyde and acetaldehyde, as highly reactive substances, are prone to polymerization and cyclization reactions, leading to a reduction of 12.1% in their proportion in emissions. It is evident that the formation of formaldehyde and acetaldehyde is more significantly influenced by combustion temperature. For the CCs emitted from DVs, the proportion of formaldehyde and acetaldehyde (44.8%) is lower than that from GVs (60.1%), which is due to the ignition method of DVs that allows for complete combustion of fuel, resulting in the full oxidation of aldehyde and ketone compounds (Saliba et al., 2017; Guo, 2023). In

330   contrast, AM using the same fuel exhibits a higher proportion of formaldehyde and acetaldehyde (57.9%) compared to DVs (44.8%), which may be due to the stricter emission standards and exhaust treatment technologies adopted by on-road vehicles. Consequently, despite using the same fuel, AM demonstrates a higher proportion of formaldehyde and acetaldehyde in its emissions.

The formation of acetone and aromatic aldehydes is significantly influenced by different fuel types. For instance, the proportion

335   of acetone and aromatic aldehydes in RCC (20.9%) is higher than that in BB (10.0%), and this difference is mainly related to the chemical composition of the fuel. Residential coal is noted to contain a higher concentration of aromatic compounds, providing abundant precursors for the formation of acetone and aromatic aldehydes(Liu et al., 2022). With increasing temperature, the proportions of acetone and aromatic aldehydes in BB and RCC increase from 6.3%, 22.5% to 26.0%, 29.6%, respectively. Under high-temperature conditions, small molecule substances are more likely to undergo polymerization and

340   cyclization reactions, leading to generation of a greater number of aromatic hydrocarbon compounds (Zhao et al., 2019). Similarly, the proportion of acetone and aromatic aldehydes in emissions from mobile sources, especially DVs, is found to be

the highest (25.7% to 42.3%), possibly due to higher content of aromatic hydrocarbons in diesel (29% to 34%), which oxidize at high temperatures to form acetone and aromatic aldehydes. Unlike the aforementioned CCs species, combustion temperature and fuel types have an impact on the emissions of unsaturated aldehydes. For example, the emission characteristics of

345 unsaturated aldehydes differ notably. Owning to the presence of unsaturated bonds, unsaturated aldehydes have higher reactivity and cannot exist stably under high-temperature conditions, leading to a decrease in their proportion from 8.6% to 2.5% under high-temperature conditions. However, in non-road sources, the proportion of unsaturated aldehydes is observed to increases by approximately 20.4% with the increase in the proportion of biodiesel blending. This phenomenon can be explained by the chemical characteristics of biodiesel. Studies have shown that glycerol in biodiesel dehydrates and condenses

350 to form acrolein under high-temperature conditions (Abdullah, 2022; Corma et al., 2008), resulting in an increase in the proportion of unsaturated aldehyde substances with the increase in the proportion of biodiesel.
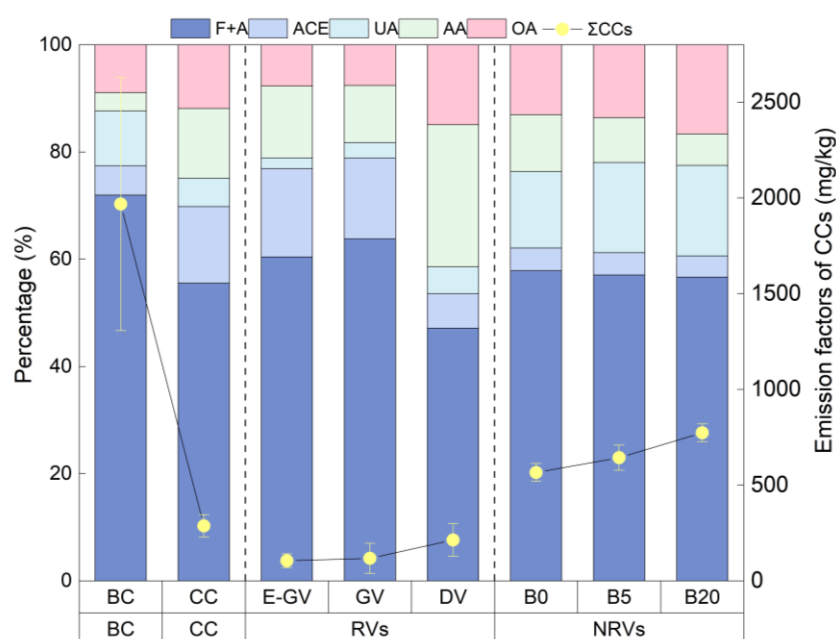
Figure 4: Differences in CCs emission characteristics and composition of four typical combustion sources; RV, on-road vehicle;
355 **NRV, non-road vehicle.**

3.4.2 Comparison of OFPs for CCs from Different Combustion Sources

In this study, the selection was made for calculation of the top ten carbonyl compounds (CCs) that have the greatest impact on ozone formation potentials (OFPs), which include formaldehyde, acetaldehyde, acetone, acrolein, propanal, crotonaldehyde,

360 butanal, cyclohexanone, isopentanal, and pentanal. As illustrated in Fig. 5, significant differences are observed in the

distribution of OFPs for the top ten CCs emanating from various combustion sources. The OFPs from BB sources (8.8 g O₃/kg-fuel) are found to be significantly higher than those from other sources ($p < 0.05$), being approximately 3.1 to 12.9 times higher than other sources, thereby indicating a substantial contribution of BB sources to the potential for ozone formation. The next highest OFPs are from non-road agricultural machinery (AM) sources (2.5 g O₃/kg-fuel), which are significantly higher than

365   those from residential coal combustion (RCC) sources (1.3 g O₃/kg-fuel) and on-road sources (0.4 to 1.1 g O₃/kg-fuel). Furthermore, it is noted that the species with high OFPs from all combustion sources are predominantly low-carbon CCs, such as formaldehyde and acetaldehyde, a finding that is consistent with other studies (Dong et al., 2014). This consistency further confirms that low-carbon CCs exhibit stronger reactivity and are present at higher concentrations in the atmosphere.

In on-road sources, the OFPs for E-GVs, GVs, and DVs are 0.4, 0.6, and 1.1 g O₃/kg-fuel, respectively. When compared to

370   pure gasoline, it has been found that the use of ethanol-blended gasoline can lead to the reduction in OFPs by 31.0% (Yao et al., 2011). This reduction is attributed to the fact that the CCs produced by E-GV contain a higher proportion of acetaldehyde, which possesses a lower maximum incremental reactivity (MIR) value (4.10) in comparison to formaldehyde (6.71). Consequently, while the use of ethanol-blended gasoline does not significantly diminish CCs emissions, it does contribute to a reduction in the reliance on fossil fuels and, to a certain extent, aids in diminishing the contribution of on-road sources to

375   atmospheric oxidizing capacity. The OFPs obtained for GVs in this study are slightly higher than those reported by Cao et al. (2016) (0.5 g O₃/kg-fuel), while the OFPs for DVs is similar to the findings of Dong et al.(2014) (1.1 g O₃/kg-fuel) but slightly lower than that reported by Yao et al. (2015)(1.5 g O₃/kg-fuel). These differences may be related to the selection of MIR values, vehicle types, and driving distances (Wang et al., 2013), all of which can affect the composition of CCs and subsequently influence the OFPs values.

380   For AM, the utilization of biodiesel also exerts a significant impact on OFPs values. As shown in Fig. 5, the OFPs of B20 (3.5 g O₃/kg-fuel) is 1.4 times that of B0 (2.5 g O₃/kg-fuel), indicating that the use of biodiesel enhances the OFPs, thereby increasing atmospheric oxidizing capacity. In the emissions of CCs from AM, formaldehyde, acetaldehyde, and acrolein are identified as the primary contributors to ozone formation, with formaldehyde being the most significant contributor, accounting for 56.3% to 57.9% of the total OFPs. With the increase in the proportion of biodiesel blending, the contribution of

385   formaldehyde slightly decreases, while the contributions of acetaldehyde, propanal, and acrolein increase by 24.0%, possibly due to the presence of esters and glycerol in biodiesel. Acrolein is classified as a Group III carcinogen by the International Agency for Research on Cancer of the World Health Organization. Therefore, when employing biodiesel, it is necessary to consider the impact of newly generated toxic and harmful components in the exhaust on human health. The OFPs value obtained for AM in this study is comparable to that reported by Yu et al. (2023) (2.2 g O₃/kg-fuel), and formaldehyde,

390   acetaldehyde, and acrolein are also the main contributors to the OFP of agricultural machinery(Yu et al., 2023).

Therefore, emissions from BB and AM are significant sources of regional atmospheric oxidizing capacity and require attention. Appropriate control measures should be implemented, such as continuing to implement straw burning bans and vigorously promoting the use of energy-efficient stoves, which can reduce CCs emissions and further decrease ozone formation by 97.6%, thereby reducing atmospheric oxidizing capacity. For AM, timely updates to emission standards (resulting in the 62.6%

395   reduction in OFPs) can effectively decrease ozone formation, and efforts should be accelerated to explore new alternative fuels

to reduce CCs emissions and lower atmospheric oxidizing capacity. Although biodiesel has good emission reduction effects

on other conventional pollutants, it increases the proportion of some toxic components and atmospheric oxidizing capacity.
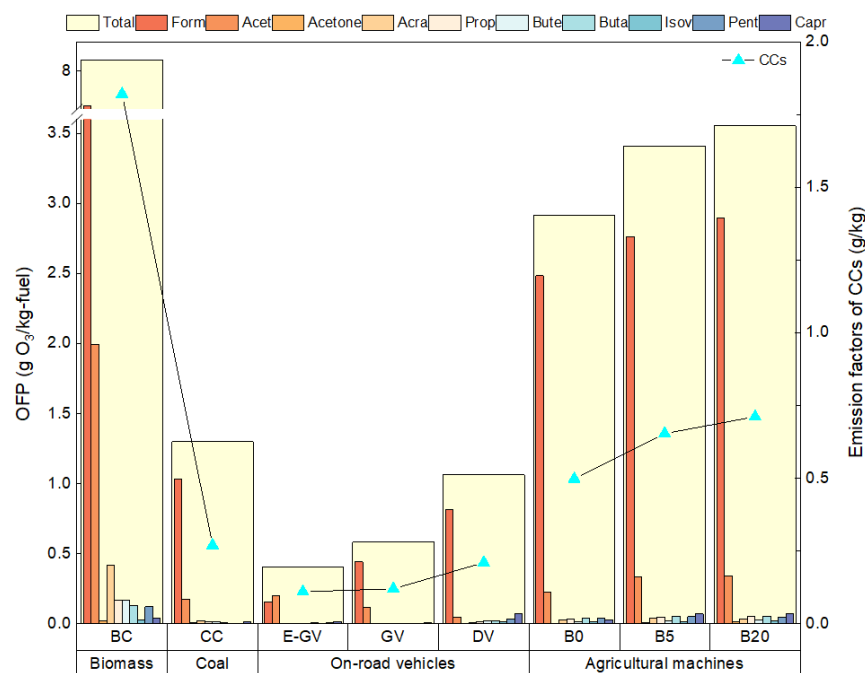
Figure 5: Ozone formation potentials (OFPs) of the top ten carbonyl compounds emitted by different combustion sources.

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4 Conclusions and Implication

The emission characteristics of CCs from RSFC, on-road sources, and non-road AM sources are found toexhibit significant

differences. Specifically, the EFs of CCs from BB (1968.2±661.2 mg/kg) are an order of magnitude higher than those from

on-road sources (117.8 to 214.1 mg/kg). Fuel types determines the composition of CCs: oxygen-rich BB sources primarily

405   emit formaldehyde and acetaldehyde (80%), which is significantly higher than other combustion sources; whereas RCC

sources, characterized by their aromatic structures, have a higher proportion of acetone and aromatic aldehydes (26.0%). In

on-road sources, the addition of ethanol-blended gasoline significantly alters the ratio of formaldehyde to acetaldehyde,

changing it from 5.6:1 to 1:1. Similarly, the use of biodiesel increases the production of unsaturated aldehydes by 20.4%,

which corresponds exactly to the 20% (v/v) addition of biodiesel.

410   For RSFC sources, the combustion temperature is identified as the key factor influencing the formation of CCs. Specifically,

improving stove technology from 500°C to 800°C (high temperature) can reduce CCs emissions by 94.6%. For on-road sources

and non-road AM sources, the raising of emission standards has been found to have the significant reduction effect on high-

emitting vehicles (61.3%). Therefore, when formulating emission reduction measures, priority should be given to updating emission standards, followed by the use of new alternative fuels (such as ethanol-blended gasoline), which can also effectively reduce CCs emissions. However, it is important to note that after implementing corresponding emission reduction measures, the proportion of some toxic compounds may increase significantly. For example, although high temperatures can enhance combustion efficiency and reduce the formation of CCs, close attention must be paid to acetone and aromatic aldehydes. High temperatures can cause small molecule substances to polymerize and cyclize, thereby promoting the formation of acetone and aromatic aldehydes, which also applies to liquid fuels. Additionally, new alternative fuels can change the composition of CCs: the use of ethanol-blended gasoline provides a large number of precursors for the formation of acetaldehyde, thereby increasing its proportion; on the other hand, the use of biodiesel promotes the formation of unsaturated aldehydes such as acrolein. Therefore, while considering combustion efficiency, attention should also be paid to the toxicity and its impact on the environment and health.

Based on the calculation of OFPs using MIR values, it has been found that BB sources (8.8 g O_3/kg-fuel) and non-road AM sources (3.5 g O_3/kg-fuel) contribute the most to the regional atmospheric OFPs, indicating that BB and AM are significant sources of atmospheric oxidizing capacity. Moreover, for AM, acrolein contributes significantly more to OFPs than other emission sources, thus highlighting the need for attention to BB sources and AM sources. Targeted control measures should be developed based on the composition of different combustion sources. At the same time, with the continuous growth in the number of on-road vehicles, the contribution of on-road sources emissions to atmospheric oxidizing capacity in the future should not be underestimated.

Data availability

All data of this study can be obtained by contact Yanli Feng(fengyanli@shu.edu.cn)

Supplement

Additional information can be found in the supporting information. Table S1 provide details on the volatile content values of six raw coals. Table S2-S4 provide the basic information of on-road sources and non-road sources sampling vehicles, respectively. Table S5 provide details on the values of MIR. Text S1 provide the quality assurance/ quality control (QA/QC).

Author contributions

LYJ, FYL and CYJ designed this study. LYJ, PY and JMJ carried them out and completed the measurement of carbonyl compounds of all samples. LYJ wrote this manuscript with contributions from all co-authors. FYL, CYJ and CT revised this manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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