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Real-world emission characteristics of carbonyl compounds from agricultural machines based on a portable emission measurement system

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ABSTRACT

Emissions of carbonyl compounds from agricultural machines cannot be ignored. Carbonyl compounds can cause the formation of ozone (O_3) and secondary organic aerosols, which can cause photochemical smog to form. In this study, 20 agricultural machines were tested using portable emission measurement system (PEMS) under real-world tillage processes. The exhaust gases were sampled using 2,4-dinitrophenylhydrazine cartridges, and 15 carbonyl compounds were analyzed by high-performance liquid chromatography. Carbonyl compound emission factors for agricultural machines were 51.14–3315.62 mg/(kg-fuel), and were 2.58 ± 2.05, 0.86 ± 1.07 and 0.29 ± 0.20 g/(kg-fuel) for China 0, China II and China III emission standards, respectively. Carbonyl compound emission factor for sowing seeds of China 0 agricultural machines was 3.32 ± 1.73 g/(kg-fuel). Formaldehyde, acetaldehyde and acrolein were the dominant carbonyl compounds emitted. Differences in emission standards and tillage processes impact ozone formation potential (OFP). The mean OFP was 20.15 ± 16.15 g O_3/(kg-fuel) for the China 0 emission standard. The OFP values decreased by 66.9% from China 0 to China II, and 67.4% from China II to China III. The mean OFP for sowing seeds of China 0 agricultural machines was 25.92 ± 13.84 g O_3/(kg-fuel). Between 1.75 and 24.22 times more ozone was found to be formed during sowing seeds than during other processes for China 0 and China II agricultural machines. Total carbonyl compound emissions from agricultural machines in China was 19.23 Gg in 2019. The results improve our understanding of carbonyl compound emissions from agricultural machines in China.

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Introduction

Carbonyl compounds are oxygenated volatile organic compounds. Aldehydes and ketones are very reactive compounds. Carbonyl compounds in the atmosphere can cause ozone (O_3) and secondary organic aerosols to form, and therefore lead to the formation of photochemical smog (Volkamer et al., 2010; Shen et al., 2013; Mellouki et al., 2015; Zhang et al., 2019; Shen et al., 2021a). Carbonyl compounds can be harmful to human health and some may be carcinogenic and mutagenic. Formaldehyde can irritate the upper respiratory tract and can affect health after acute or chronic exposure through inhalation and through other forms of exposure, including through the eyes, nasopharynx, and throat. Formaldehyde was included in the first list of human carcinogens by the International Agency for Research on Cancer (Cogliano et al., 2011; Luecken et al., 2018). Acetaldehyde can cause digestive tract diseases (Ho et al., 2015), and acrolein can damage the cardiovascular system, and cause cardiomyopathy and cardiac failure (Henning et al., 2017).

Fossil fuel combustion has been found to be an important source of carbonyl compounds (Chen et al., 2014; Zhang et al., 2019). Most previous studies of carbonyl compound emissions caused by mobile fossil fuel combustion sources have been focused on on-road mobile sources. Schauer et al. (1999) and Jakober et al. (2008) measured carbonyl compound emissions from gasoline- and diesel-powered vehicles on chassis dynamometers in California, (USA). Grosjean et al. (2001), Ho et al. (2007), Ban-Weiss et al. (2008) and Zhang et al. (2016b) estimated the emission of carbonyl compounds from gasoline, diesel and liquefied petroleum gas vehicles by tunnel tests in Pennsylvania, Hong Kong, San Francisco and Guangzhou, respectively. Zhang et al. (2013), Ye (2014), Yao et al. (2015a, 2015b, 2015c) and Cao et al. (2016, 2020) evaluated carbonyl compound emissions from gasoline vehicles and diesel trucks using portable emission measurement systems (PEMS) under real-world conditions in Beijing and Xiamen. Various methods were used to measure carbonyl compound emissions from vehicles in the studies mentioned above, and the results indicated the severity of carbonyl compound pollution caused by vehicles. The Chinese government has recently adopted measures to decrease emissions of pollutants from mobile sources on roads. For example, emission standards have been formulated and implemented, and environmental supervision of design, finalization, production and sales for newly produced vehicles has been strengthened (Wu et al., 2011; Zhang et al., 2014; Yue et al., 2015; Wu et al., 2016). Environmental management of road mobile sources has given good initial results, and attention is now being paid to the management of non-road mobile sources.

In 2020, non-road mobile sources emitted 425 Gg of hydrocarbons (HCs), which was 22.3% of emissions from mobile sources on roads (MEE, 2021). Agricultural machines are the most important non-road mobile sources, accounting for 48.0% of total emissions from non-road mobile sources in 2020 (MEE, 2021). China is a large country with a strong agriculture industry. Grain was cultivated on 116.77×10^6 ha in China in 2020, and the total grain output was 669.49×10^6 ton (NBSC, 2021). The number of agricultural machines used in China has been increasing each year for many years, and the overall agricultural mechanization rate and wheat-production mechanization rate were 76.7% and 97.2%, respectively, in 2020 (MOA, 2021). Agricultural machines are routinely used for transportation, planting, and harvesting but are generally not technologically advanced, have long service lives and high fuel consumptions, and are poorly maintained. Li et al. (2019) found that emissions during tillage processes play important roles in causing seasonal severe pollution events in intensively agricultural areas in China. Between 1997 and 2015, volatile organic compounds emitted by agricultural machines accounted for 8.9%–59.1% of total gas emissions during tillage processes, and 59% of volatile organic compound emissions from agricultural machines occurred in North China (Li et al., 2019). However, carbonyl compound emissions from agricultural machines have been studied little. Yao et al. (2015c) measured the emission of carbonyl compounds from rural vehicles in rural areas of Beijing, China using PEMS and found that severe carbonyl compound pollution was caused by agricultural machines. Carbonyl compound emissions from agricultural machines such as tractors are still not understood.

The main aim of this study was to acquire the emission characteristics of carbonyl compounds for agricultural machines during real tillage process in China. We tested 20 agricultural machines complying with different emission standards during different tillage processes using a PEMS in China. Carbonyl compounds were collected using 2,4-dinitrophenylhydrazine (2,4-DNPH) adsorption cartridges, and then qualitatively and quantitatively determined by high-performance liquid chromatography (HPLC). Carbonyl compound emission factors were then calculated using measured fuel consumption data for the tested agricultural machines. Carbonyl compound emissions from agricultural machines were then characterized in relation to various influencing factors, including emission standards and tillage processes. The ozone formation potentials (OFPs) of the agricultural machines that were tested were then calculated, and total carbonyl compound emissions from agricultural machines in China were estimated. The results will help decision makers develop strategies for decreasing pollution caused by agricultural machines, improve our understanding of the potential effects of agricultural machines on ozone formation, and support the achievement of carbon neutrality in China.

1. Materials and methods

1.1. *Sampling system and method*

A combined PEMS was used to measure carbonyl compound emissions from agricultural machines under real-world tillage processes. The PEMS had four main components: a SEMTECH-LDV gas analyzer (Sensors, Ann Arbor, MI, USA), a SEMTECH-EFM exhaust flowmeter (Sensors, Ann Arbor, MI, USA), a CTM-039 fine particulate matter (FPM) constant-velocity sampling dilution system (Environmental Supply Company, Durham, North Carolina, USA) and a carbonyl compound sampling unit, as shown in Fig. 1. The carbonyl compound sampling unit

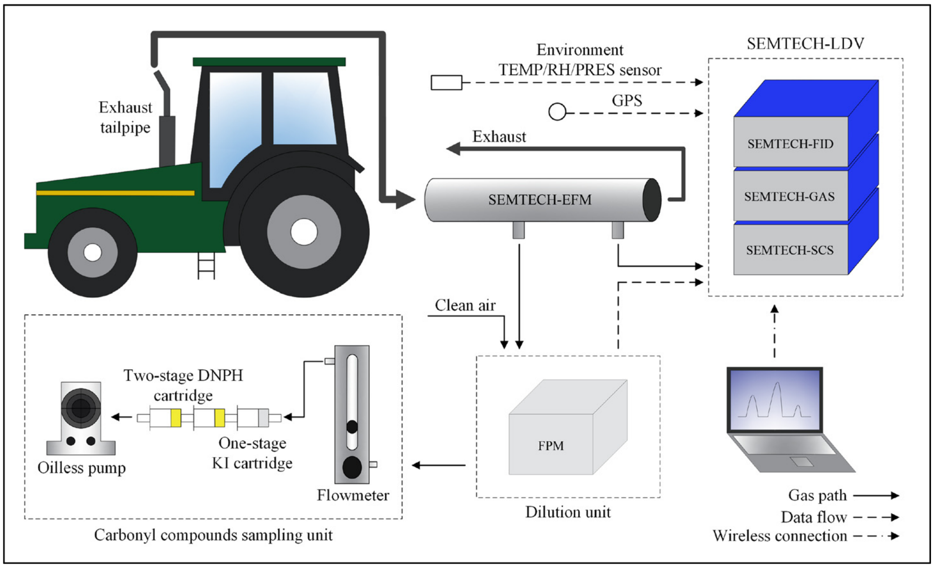

Fig. 1 – Schematic of the portable emission measurement system for sampling carbonyl compounds emitted by an agricultural machines.

contained a one-stage potassium iodide (KI) cartridge (Bonna-Agela Technologies, China), a two-stage 2,4-DNPH cartridge (Bonna-Agela Technologies Inc., China), an oil-free pump at the rear, and a rotameter at the front. The 2,4-DNPH adsorption cartridge was located downstream of the scrubber containing KI, which was used to eliminate interferences caused by oxidizing substances and particulate matter. Carbonyl compounds, including aldehydes and ketones were captured by reacting with 2,4-DNPH during the sampling process. The system was described in more detail in previous publications (Yao et al., 2011, 2015b; Huo et al., 2012; Shen et al., 2014, 2021c; Wu et al., 2015; Cao et al., 2016, 2020).

1.2. Agricultural machines testing and operating modes

A total of 20 agricultural machines, including 14 tractors and 6 combine harvesters, were tested in Jining, Shandong Province, China. The agricultural machines selected for this study was representative agricultural machines used in the actual tillage process and the emission standards. The machines that were tested were built between 1988 and 2019. Four machines did not comply with any emission standard (labeled China 0), nine complied with the China II emission standard, and seven complied with the China III emission standard. Agricultural machines that complied with the China I emission standard were not tested because this emission standard was implemented for only a short period, and thus only a small proportion of agricultural machines comply with it. Agricultural machines were tested during six tillage processes. The processes were tilling, plowing, sowing, harvesting, return and pesticide spraying. More detailed information is provided in Table 1. The agricultural machines were leased from private owners or large agricultural machines service center and were tested under normal tillage processes. None of the machines was equipped with an exhaust gas treatment device and each machine used diesel, which is the main fuel used by agricultural machines (MEE, 2021).

The PEMS was placed on a platform behind the tailpipe of the agricultural machine being tested. The experimenter operated and monitored the PEMS when the agricultural machine was operating. The agricultural machines were tested when they were being used for tillage processes in August and September 2020.

1.3. Analysis of carbonyl compounds

Each two-stage cartridge was separated and each stage was eluted separately with acetonitrile to allow the carbonyl compounds to be identifies readily. Each extract was diluted to 5 mL with acetonitrile in a volumetric flask. The pretreatment method was previously described by Zhang et al. (2013) and Cao et al. (2020). Carbonyl compounds were trapped on the cartridges by reacting with 2,4-DNPH. The 2,4-DNPH derivatives of the carbonyl compounds were qualitatively and quantitatively analyzed by high-performance liquid chromatography using an external standards method. Fifteen carbonyl-DNPH derivatives provided by Supelco (TO-11/IP-6A Mix, Supelco, USA) were used as standard samples for analysis. The separation column was an Agilent HC-C18(2) (4.6 × 250 nm, ID 5 µm), and the mobile phase was acetonitrile and pure water, with the gradient procedures, as shown in Table 2. The column temperature was 25°C, and the flow rate was 1.0 mL/min, the injection volume was 20 µL. The detection wavelength was 360 nm.

1.4. Emission factors calculation

The carbonyl compound emission factors (g/(kg-fuel)) based on fuel consumption were calculated in using Eq. (1) (Cao et al.,

Table 1 – Information about the agricultural machines that were tested.

Test number	Machinery type	Vehicle model	Model year	Tillage process	Emission standard	Engine power (kW)
AM01	Small Tractor	Xinhu	1997	Pesticide spraying	China 0	13.3
AM02	Medium Tractor	Shanghai	1992	Sow	China 0	36
AM03	Medium Tractor	Lovol	2005	Sow	China 0	43
AM04	Medium Tractor	Shanghai	1988	Sow	China 0	51.5
AM05	Medium Tractor	Fubaotian	2014	Sow	China II	29.4
AM06	Medium Tractor	Taishan	2015	Sow	China II	29.4
AM07	Medium Tractor	Qingtuo	2013	Sow	China II	59
AM08	Medium Tractor	Dongfanghong	2013	Tilling	China II	66.2
AM09	Medium Tractor	Dongfanghong	2013	Tilling, Plow, Sow, Return	China II	73.5
AM10	Large Tractor	Shuhe	2016	Plow	China II	103
AM11	Combine harvester	Chunyu	2014	Harvest	China II	75
AM12	Combine harvester	Chery guwang	2014	Harvest	China II	92
AM13	Combine harvester	Lovol	2016	Harvest	China II	107
AM14	Large Tractor	Lovol	2016	Tilling	China III	102.9
AM15	Large Tractor	Shuhe	2013	Tilling	China III	103
AM16	Large Tractor	Taishan	2016	Plow	China III	110.3
AM17	Large Tractor	Changfa	2019	Plow	China III	147
AM18	Combine harvester	Chunyu	2017	Harvest	China III	113
AM19	Combine harvester	Chunyu	2019	Harvest	China III	118
AM20	Combine harvester	Golddafeng	2019	Harvest	China III	118

Table 2 – Mobile phase gradient used for the high-performance liquid chromatography analyses.

Time (min)	Acetonitrile (%)	Pure water (%)
0-25	50.00	50.00
25-61	60.00	40.00
61-70	50.00	50.00

2020):

$$\mathrm{EF_i} = \frac{(\mathrm{C_{1i}} \times V_{1e} + \mathrm{C_{2i}} \times V_{2e}) \times \mathrm{DR} \times V_g}{V_s \times F} \times 10^{-6} \quad (1)$$

where, $\mathrm{EF_i}$ (g/(kg-fuel)) is the emission factor of carbonyl compound *i*, $\mathrm{C_{1i}}$ and $\mathrm{C_{2i}}$ (µg/mL) are the concentrations of carbonyl compound *i* in the first and second cartridge eluates, respectively, V_{1e} and V_{2e} (mL) are the eluent volumes for the first and second cartridges, respectively, *DR* is the dilution ratio of the exhaust gas, V_g (L) is the total volume of exhaust gas during the entire test, V_s (L) is the volume of sample that flowed through the cartridge and *F* (kg-fuel) is the fuel consumption of the agricultural machines during the testing process. The emission factor for carbonyl compound *i* was calculated by dividing the total amount of carbonyl compound *i* emitted by the amount of fuel consumption during the test period.

1.5. *OFP Calculation*

The OFP based on the carbonyl compound emission factors was calculated using the maximum incremental reactivity (MIR) method, as shown in Eq. (2):

$$\mathrm{OFP_i} = \mathrm{EF_i} \times \mathrm{MIR_i} \quad (2)$$

where, $\mathrm{OFP_i}$ ((g O_3)/(kg-fuel)) is the OFP of carbonyl compound i, $\mathrm{EF_i}$ (g/(kg-fuel)) is the emission factor of carbonyl compound i, and MIR_i is the maximum incremental reactivity value of carbonyl compound *i* (Carter, 2010). The MIRs for various carbonyl compounds are shown in Table S1.

1.6. *Calculation of total emissions*

Eq. (3) was used to calculate the total carbonyl compounds emissions for agricultural machines in 2019 (MEE, 2014):

$$E_y = \sum \left(\mathrm{EF}_{i,j,k} \times A_y \times P_{j,k}\right) \times 10^{-9} \quad (3)$$

where, E_y (Gg) is the total emissions of carbonyl compounds in area *y*, $\mathrm{EF}_{i,j,k}$ (g/(kg-fuel)) is the emission factor for carbonyl compound *i* for tillage process *j* for emission standard *k*, A_y (kg) is the fuel consumption in area *y*, which was summarized from the China Rural Statistical Yearbook for 2020 (NBSC, 2020a) and shown in Table S2, and $P_{j,k}$ is the proportional coefficient for tillage process *j* for a machine complying with emission standard *k*.

The proportional coefficient was used to subdivide the fuel consumption into different emission standards and tillage processes. The proportional coefficients were based on the proportions of fuel consumed by agricultural machines used for different tillage processes and the proportions of agricultural machines complying with different emission standards. The fuel consumptions of agricultural machines used for different tillage processes were taken from the results of a previous field survey (Kong, 2021). The numbers of agricultural

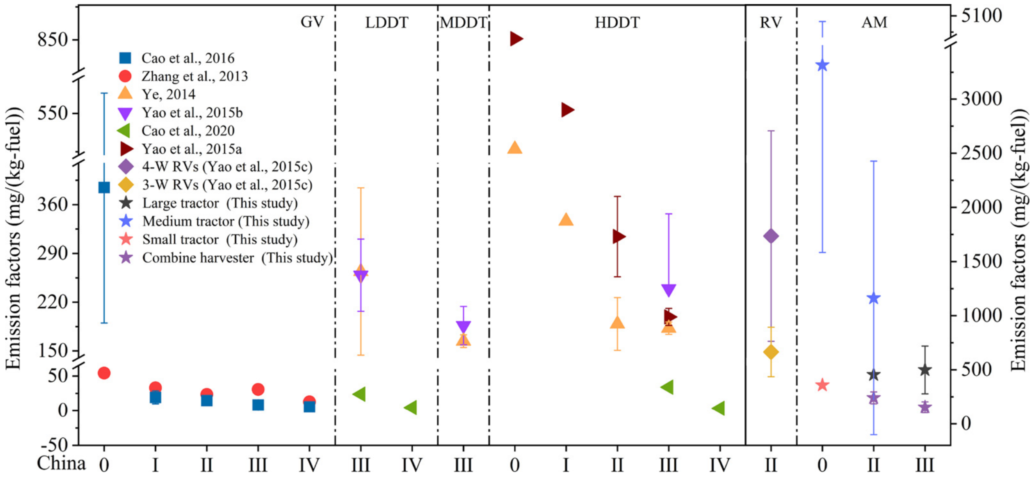

Fig. 2 – Carbonyl compound emission factors for agricultural machines (tested in this study) and other machines (tested in previous studies).

Note: The carbon balance method was used to convert emission factors based on mileage from other publications into emission factors based on fuel consumption. GV, LDDT, MDDT, HDDT, RV, AM, 3-W, and 4-W are gasoline vehicles, light-duty diesel trucks, medium-duty diesel trucks, heavy-duty diesel trucks, rural vehicles, agricultural machines, 3-wheel vehicles, and 4-wheel vehicles, respectively.

machines complying with different emission standards were determined using a survival curve and the numbers of agricultural machines in different regions, published in relevant statistical yearbooks. This survival curve method allowed the distributions of agricultural machines complying with different emission standards to be simulated (Shen et al., 2021b; NBSC, 2020a).

1.7. *Uncertainty analysis*

The 95% confidence interval (CI) and coefficient of variation (CV) were calculated using Eqs. (4) and (5) (Wang et al., 2016):

$$\mathrm{CI}_x = \mu_x \pm 1.96\frac{\sigma_x}{\sqrt{n}} \tag{4}$$

$$\mathrm{CV}_x = \frac{\sigma_x}{\mu_x} \tag{5}$$

where, CI_x is the confidence interval of emission factors x, CV_x is the coefficient variation of emission factors x, μ_x is the arithmetic average of emission factors x, σ_x is the standard deviation of emission factors x, n is the number of emission factors x.

2. Results and discussion

2.1. *Emission of carbonyl compounds and comparison with other research*

A total of 15 carbonyl compounds were identified in the samples. The carbonyl compound emission factors for agricultural machines were 51.14–3,315.62 mg/(kg-fuel) (Fig. 2). The emission factors may have varied strongly because of the different types of machines that were tested, the different emission standards the machines complied with, and the different tillage processes. In terms of machines type, the carbonyl compound emissions of China 0 medium tractor were 9.25 times higher than those of China 0 small tractor. For China II, the carbonyl compound emissions of medium tractor were 2.56 and 4.83 times higher than those of large tractor and combine harvester, respectively. And for China III, the carbonyl compound emissions of large tractor were 3.26 times higher than those of combine harvester. The effects of emission standards and tillage processes on carbonyl emission factors will be further explained in the following section.

The percentage contributions of the emission factors of the separate carbonyl compounds to the total carbonyl compound emission factors for the agricultural machines that were tested are shown in Table 3. The low-molecular-weight carbonyl compounds formaldehyde, acetaldehyde, and acrolein were the dominant carbonyl compounds emitted from the agricultural machines, and together contributing 73.1%–85.2% of the total carbonyl compound emission factors. Similar results were found in previous studies of diesel vehicles. Siegl et al. (1999) found that formaldehyde and acetaldehyde contributed 74% of the total carbonyl compound emissions from a light-duty diesel vehicle. Ban-Weiss et al. (2008) found that formaldehyde, acetaldehyde and acrolein contributed 81.6% of carbonyl compounds from diesel-powered motor vehicles in San Francisco. Yang et al. (2015) observed that formaldehyde, acetaldehyde and acrolein contributed 92.9% of total carbonyl compounds from diesel-powered generators. Cao et al. (2020) found that formaldehyde, acetaldehyde and acrolein contributed 71.9% of carbonyl compounds from diesel trucks.

The differences between the carbonyl compound emission factors found in this study and previous studies are shown in Fig. 2. Much higher emission factors were found for agricultural machines than were previously found for gasoline vehicles and light-, medium-, and heavy-duty diesel trucks. The carbonyl compound emissions were 8.37 times higher for

Table 3 – Emission factor percentages of carbonyl compounds from tested agricultural machines.

Carbonyl compounds	Mass percentages ± standard deviation (%)									
	China 0		China II					China III		
	Sow	Pesticide spraying	Sow	Tilling	Plow	Harvest	Return	Plow	Tilling	Harvest
Formaldehyde	62.23 ± 9.82	63.90	60.15 ± 2.99	57.94 ± 11.72	52.41 ± 6.67	52.85 ± 4.91	66.66	60.56 ± 4.56	50.14	44.24 ± 9.25
Acetaldehyde	13.93 ± 2.79	12.48	16.39 ± 2.10	17.00 ± 3.86	16.35 ± 0.83	17.02 ± 2.55	12.48	15.53 ± 1.64	14.18	17.17 ± 5.30
Acrolein	3.34 ± 3.64	5.13	5.10 ± 4.08	6.73 ± 1.07	8.54 ± 1.70	9.49 ± 2.59	6.09	5.94 ± 3.04	13.81	11.69 ± 4.80
Acetone	5.08 ± 2.12	1.91	1.92 ± 1.84	3.20 ± 1.80	1.43 ± 0.61	1.57 ± 1.18	-	1.73 ± 1.45	0.68	1.18 ± 0.44
Propionaldehyde	3.41 ± 1.54	2.61	3.83 ± 0.60	3.24 ± 1.58	3.83 ± 0.60	3.30 ± 0.21	-	3.29 ± 0.26	1.71	2.54 ± 0.25
Crotonaldehyde	1.77 ± 0.10	1.00	0.80 ± 0.40	0.94 ± 0.78	0.97 ± 0.23	0.81 ± 0.49	0.60	0.97 ± 0.06	0.69	0.36 ± 0.14
Butyraldehyde	2.49 ± 0.82	3.72	2.54 ± 0.38	2.36 ± 0.66	2.67 ± 0.22	2.66 ± 0.29	1.26	2.30 ± 0.49	3.24	2.66 ± 0.54
Benzaldehyde	2.15 ± 0.49	3.18	2.66 ± 1.02	1.98 ± 0.36	3.04 ± 1.82	2.87 ± 0.96	3.73	2.86 ± 0.12	4.66	4.77 ± 2.97
Isovaleraldehyde	0.97 ± 0.45	1.57	1.11 ± 0.47	1.14 ± 0.67	2.26 ± 0.31	2.26 ± 0.61	3.44	1.44 ± 0.18	4.75	2.47 ± 0.14
Valeraldehyde	1.64 ± 0.69	2.21	1.15 ± 0.51	1.68 ± 0.64	2.52 ± 0.45	1.97 ± 0.45	2.98	1.59 ± 0.21	2.19	2.36 ± 0.83
o-Tolualdehyde	0.59 ± 0.39	0.93	0.53 ± 0.15	0.18 ± 0.25	0.10 ± 0.14	0.51 ± 0.39	2.64	0.78 ± 0.20	-	1.09 ± 1.81
m-Tolualdehyde	0.37 ± 0.31	1.17	0.80 ± 0.21	0.84 ± 0.45	2.24 ± 1.42	1.02 ± 0.89	-	0.77 ± 0.53	2.80	2.49 ± 3.66
p-Tolualdehyde	0.76 ± 0.44	-	2.07 ± 1.47	1.13 ± 0.90	0.89 ± 0.55	1.64 ± 0.96	-	1.03 ± 1.09	-	3.32 ± 1.69
Hexaldehyde	1.17 ± 0.42	0.18	0.81 ± 0.56	1.54 ± 0.36	2.69 ± 0.93	1.98 ± 1.30	0.11	1.21 ± 0.52	1.14	3.67 ± 1.97
2,5-Dimethylbenzaldehyde	0.09 ± 0.16	0.00	0.14 ± 0.17	0.08 ± 0.14	0.06 ± 0.09	0.05 ± 0.08	-	-	-	0.01 ± 0.01

"-" indicates not detected.

agricultural machines than gasoline vehicles produced before Chinese emission standards were established (China 0) and 32.29 and 16.78 times higher for agricultural machines than gasoline vehicles complying with the China II and China III emission standards, respectively (Cao et al., 2016; Zhang et al., 2013). Carbonyl compounds are emitted because of incomplete oxidation of fuel during combustion (Tsai et al., 2012; Hong-li et al., 2017; Jhang et al., 2018), and there are differences in the composition and air/fuel ratios of gasoline and diesel (Grosjean et al., 2001; Yao et al., 2015b). Moreover, the quality of gasoline is higher than that of diesel in China (Wu et al., 2017). Carbonyl compound emissions were 1.79 times higher for China III agricultural machines than China III light-duty diesel trucks (Ye, 2014; Yao et al., 2015b; Cao et al., 2020). Carbonyl compound emissions were 1.86 times higher for China III agricultural machines than China III medium-duty diesel trucks (Ye, 2014; Yao et al., 2015b). In addition, the carbonyl compound emissions from agricultural machines were 2.72, 2.46 and 1.99 times higher than those from heavy-duty diesel trucks for China 0, China II and China III, respectively (Ye, 2014; Yao et al., 2015a, 2015b; Cao et al., 2020). This may be due to the differences in factors such as fuel quality, driving cycles, engine technology and exhaust control technology. Agricultural diesel is a poorer quality than automotive diesel (MEE, 2021), and more advanced engines and post-processing systems are used in diesel trucks than agricultural machines (Yao et al., 2015c). In fact, agricultural machines currently used in China can only meet the China I–III emission standards by using higher quality fuel and lubricants, alternative fuels, optimized gas distribution systems, and optimized combustion chamber shapes (Tan et al., 2018). The China IV emission standard for non-road mobile machines, which will be implemented in December 2022, will require off-board exhaust post-processing techniques such as exhaust gas recirculation, selective catalytic reduction, and diesel particulate filters (Tan et al., 2018).

It is worth noting that carbonyl compound emissions from rural vehicles were different from the other vehicles mentioned above. Carbonyl compound emissions from China II agricultural machines were found to contribute 51.6% of carbonyl compound emissions from China II rural vehicles. Furthermore, carbonyl compound emissions from 4-wheel rural vehicles were similar to carbonyl compound emissions from China 0 agricultural machines, and carbonyl compound emissions from 3-wheel rural vehicles were similar to carbonyl compound emissions from China II agricultural machines (Yao et al., 2015c). These results indicated the gradual increase in vehicle pollution problems in rural areas that have occurred. Rural vehicles and agricultural machines are used often in rural areas. Rural vehicles are mainly used to transport vegetables and other goods, and agricultural machines are mainly used for farming. Moreover, during the farming season, agricultural machines are often used at low speeds and with high loads and thus emit high short-term emission amounts of carbonyl compounds than other vehicles. Fu et al. (2013) found HC emission factors of 6.62–16.39 g/(kg-fuel) for tractors. Ge et al. (2013) found HC emission factors of 11.4–11.5 g/(kg-fuel) for combine harvesters. Huang et al. (2018) found volatile organic compound emission factors of 2.4–13.6 g/(kg-fuel) for agricultural machines. Wang et al. (2020) found HC emission factors of 5.20–36.87 and 9.38–11.86 g/(kg-fuel) for tractors and combine harvesters, respectively. The carbonyl compound emission factors for agricultural machines we found accounted for 0.4%–28.8% of the emission factors for agricultural machines found in the studies mentioned above.

2.2. *Influencing factors of carbonyl compound emissions from agricultural machines*

2.2.1. *Emission standards*

The carbonyl compound emission factors for agricultural machines complying with different emission standards are shown in Fig. 3a. The carbonyl compound emission factors for China 0, China II, and China III agricultural machines were 2.58 ± 2.05, 0.86 ± 1.07, and 0.29 ± 0.20 g/(kg-fuel), respectively. The formaldehyde emission factors for China 0, China II, and China III agricultural machines were 1.66 ± 1.46, 0.51 ± 0.67, and 0.16 ± 0.13 g/(kg-fuel), respectively. The acetaldehyde emission factors for China 0, China II, and China III agricultural machines were 0.33 ± 0.22, 0.15 ± 0.20, and 0.05 ± 0.03 g/(kg-fuel), respectively. The acrolein emission factors for China 0, China II, and China III agricultural machines were 0.07 ± 0.06, 0.04 ± 0.03, and 0.02 ± 0.01 g/(kg-fuel), respectively.

Stricter emission standards decreased the carbonyl compound emission factors. The carbonyl compound emission factors were 66.5% lower for China II machines than China 0 machines. The formaldehyde, acetaldehyde, and acrolein emission factors were 69.5%, 55.6%, and 41.0% lower, respectively, for China II machines than China 0 machines. This was because the pressurized intercooling systems used in China II tractors and combine harvesters cause more uniform combustion in the engine cylinders and therefore decrease carbonyl compound emissions (Zhang et al., 2016a). The carbonyl compound, formaldehyde, acetaldehyde, and acrolein emission factors were 66.6%, 68.7%, 69.1%, and 36.4% lower, respectively, for China III machines than China II machines. This was because exhaust gas recirculation or electronically controlled common rail systems are used, in addition to pressurized intercooling systems, in China III agricultural machines (Tan et al., 2018). The mean carbonyl compositions for machines complying with different emission standards are shown in Fig. 3b. Tightening the emission standard decreased the proportion of formaldehyde emitted but increased the proportion of acrolein emitted. This may have been related to changes in the technology and fuel used. Carbonyl compounds with different MIRs could have different effects on ozone production (Carter, 2010). There is currently no carbonyl compound emission limit specified in the emission standards for non-road mobile machines in China, and existing standards contain emission limits only for CO, HCs, NO_X, and particulate matter (Yao et al., 2015a). Our results indicated that carbonyl compound emissions have gradually decreased as stricter emission standards for CO, HCs, NO_X, and particulate matter have been implemented.

2.2.2. *Tillage processes*

We classified the carbonyl compounds by the number of carbon atoms the compounds contain and then calculated carbonyl emission factors for the agricultural machines comply-

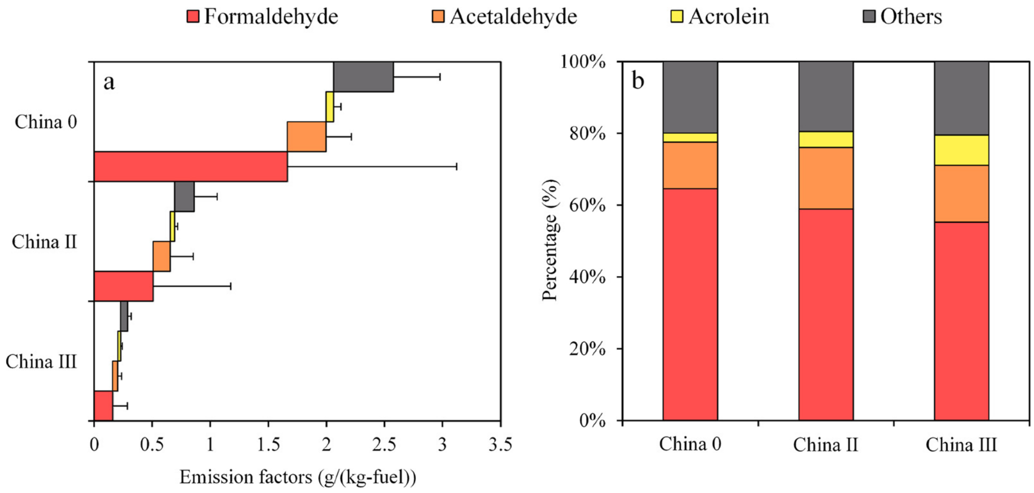

Fig. 3 – Carbonyl compound (a) emission factors and (b) mean compositions for agricultural machines complying with different emission standards.

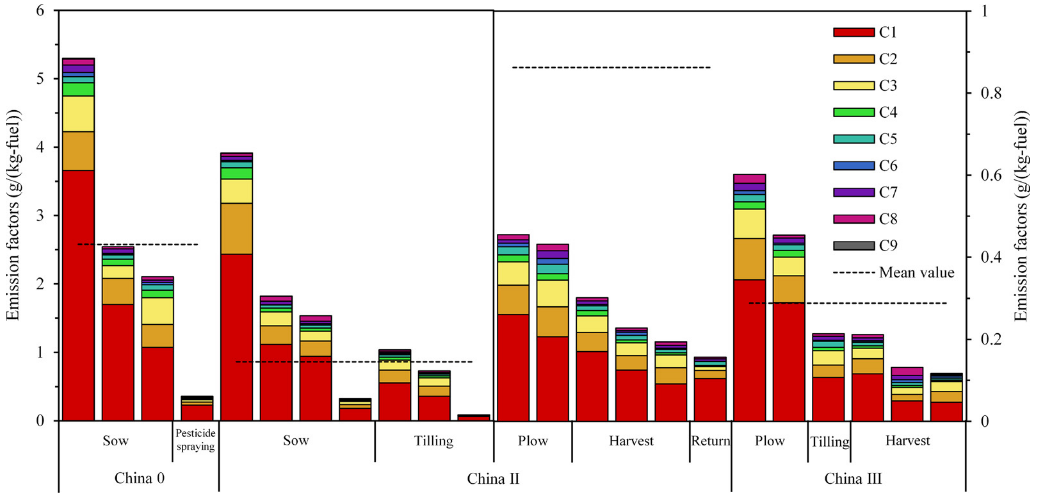

Fig. 4 – Carbonyl compound emission factors for agricultural machines complying with different emission standards and during different tillage processes.
Note: C1, formaldehyde; C2, acetaldehyde; C3, acrolein, acetone, propionaldehyde; C4, crotonaldehyde, butyraldehyde; C5, valeraldehyde, isovaleraldehyde; C6, hexaldehyde; C7, benzaldehyde; C8, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde; C9, 2,5-dimethylbenzaldehyde.

ing with different emission standards and used for different tillage processes. The results are shown in Fig. 4. Tests were performed for six tillage processes. Different carbonyl compound emission factors were found for different tillage processes. For China 0 agricultural machines, the carbonyl emission factors used for sowing and pesticide spraying were 3.32 ± 1.73, and 0.36 g/(kg-fuel), respectively. The carbonyl emission factors were 9.3 times higher during sowing than pesticide spraying. The emission factors were highest for China 0 machines because no emission limits were in force when these machines were produced. This would have been because pesticide spraying is usually a manual task or is performed using a small tractor with a low fuel consumption and low power output. For China II agricultural machines, the carbonyl emission factors used for sowing, tilling, plowing, harvesting, and returning were 1.90 ± 1.49, 0.62 ± 0.49, 0.44 ± 0.02, 0.24 ± 0.05, and 0.16 g/(kg-fuel), respectively. The carbonyl compound emission factors were reduced in the order of sowing, tilling, plowing, harvesting, and returning. This would have been because fuel consumption per unit of time would have been higher for sowing, tilling, plowing, and harvesting than for returning. And the inadequate combustion of the tractor during sowing resulted in higher carbonyl compound emissions. For China III machines, carbonyl compound emissions were 2.47 and 3.44 times higher during plowing than during tilling and harvesting, respectively. The difference between plowing and tilling tractors occurred because plows have more resistance than rototillers, resulting in higher fuel consumption and power when plowing. And the lower emissions of carbonyl compounds from combine harvesters may

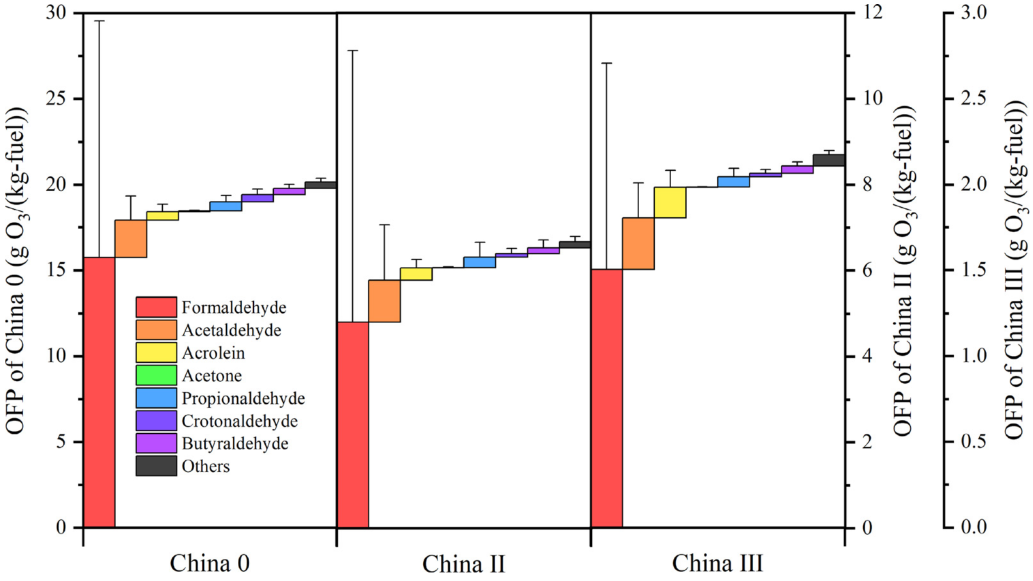

Fig. 5 – Ozone formation potentials (OFPs) of carbonyl compounds emitted by agricultural machines complying with different emission standards.

be related to the increased stability of the diesel engine from the longer sampling time.

Carbonyl compounds containing few carbon atoms were the main carbonyl species emitted by the agricultural machines. Carbonyl compounds with one carbon atom (formaldehyde), two carbon atoms (acetaldehyde), and three carbon atoms (acetone, acrolein, and propionaldehyde) were the three main components of the carbonyl compounds that were emitted, contributing 56.5%, 15.8%, and 12.6%, respectively, of total carbonyl compound emissions.

2.3. OFPs

We calculated the OFPs based on the MIR method to estimate the contribution of tested agricultural machines exhaust to photochemical ozone production (Carter, 1994). As mentioned in Section 2.1, carbonyl compound emissions were higher for the agricultural machines during tillage processes than for other vehicles. Agricultural machines may therefore be important causes of ozone formation. The OFPs for agricultural machines complying with different emission standards are shown in Fig. 5. The OFPs for China 0, China II, and China III machines were 20.15 ± 16.15, 6.67 ± 8.41, and 2.17 ± 1.59 (g O_3)/(kg-fuel), respectively. The OFPs were 66.9% lower for the China II machines than the China 0 machines and 67.4% lower for the China III machines than the China II machines. The OFPs for the agricultural machines complying with different emission standards and during different tillage processes are shown in Fig. 6. For China 0 agricultural machines, the OFPs for sowing and pesticide spraying were 25.92 ± 13.84, and 2.84 (g O_3)/(kg-fuel), respectively. For China II agricultural machines, the OFPs for sowing, tilling, plowing, harvesting, and returning were 14.83 ± 11.86, 4.64 ± 3.63, 3.33 ± 0.28, 1.83 ± 0.44, and 1.25 (g O_3)/(kg-fuel), respectively. For China III agricultural machines, the OFPs for plowing, tilling, and harvesting were 4.12 ± 0.75, 1.59, and 1.07 ± 0.46 (g O_3)/(kg-fuel), respectively. The sowing process formed 1.75 to 24.22 times more ozone than other processes for China 0 and China II agricultural machines. Formaldehyde was found to be the main carbonyl compound responsible for ozone formation because of the large amounts emitted and the high MIR of formaldehyde.

Agricultural machines have higher OFPs than other vehicles in the literature during tillage processes (Zhang et al., 2013; Cao et al., 2016, 2020; Ye, 2014; Yao et al., 2015a, 2015b, 2015c). In the previous studies, OFPs were calculated by multiplying emission factors based on fuel consumption (see Section 2.1) by the weighted mean MIRs for the carbonyl compounds of interest (MIR_m). The OFPs we found for agricultural machines and the OFPs found for other vehicles in previous studies are shown in Table 4. And the results indicated that the OFPs were much higher for agricultural machines during tillage processes (e.g., crop planting and harvesting) than for other vehicles.

2.4. *Emission of carbonyl compounds from agricultural machines in China*

Carbonyl compounds emissions from agricultural machines in China are shown in Fig. 7. Activity data (i.e., agricultural diesel use) were obtained from the China Rural Statistical Yearbook for 2020 (NBSC, 2020a). Agricultural machines in China emitted 19.23 Gg of carbonyl compounds in 2019. China 0, China I, China II, and China III machines emitted 3.75, 2.51, 10.85, and 2.12 Gg, respectively, of carbonyl compounds in 2019. China II agricultural machines emitted the largest amount of carbonyl compounds because there are more China II agricultural machines than other agricultural machines. China II machines used for sowing, tilling, harvesting, pesticide spraying, and other processes emitted 7.68, 1.88, 0.56, 0.24, and 0.49 Gg, respectively, of carbonyl compounds. Lang et al. (2018) found total HC emissions of 1,211.39 Gg for agricultural machines in China in 2014. Hou et al. (2019) found

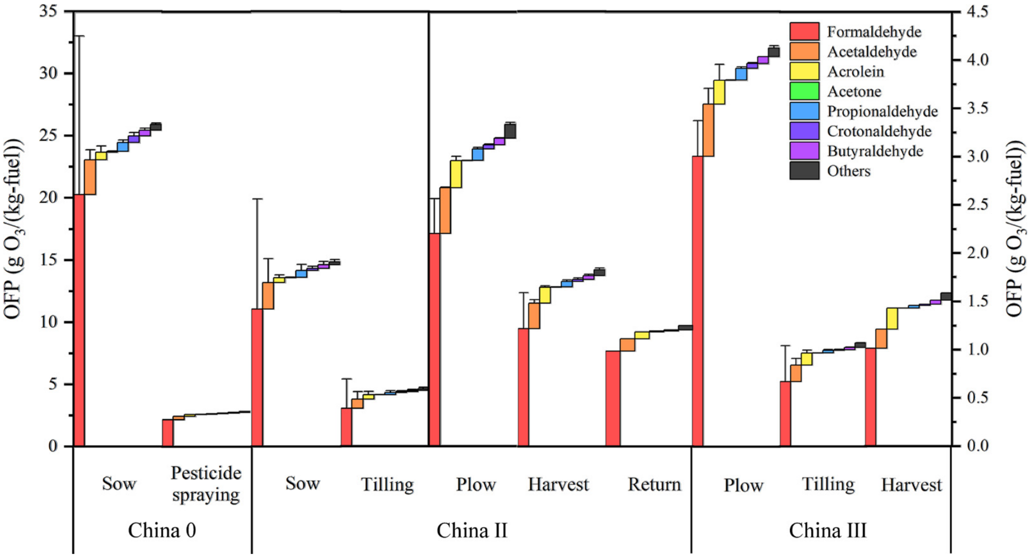

Fig. 6 – Ozone formation potentials (OFPs) of carbonyl compounds emitted by agricultural machines complying with different emission standards and during different tillage processes.

Table 4 – Ozone formation potentials (OFPs) for the agricultural machines tested in this study and for other vehicles tested in previous studies.

		OFPs (g O_3/(kg-fuel))
This study	Agricultural machines	1.07–25.92
Zhang et al., 2013	Gasoline vehicles	0.10–0.42
Cao et al., 2016		0.04–2.98
Ye, 2014	Light-duty diesel trucks	2.05
Yao et al., 2015b		2.01
Cao et al., 2020		0.04–0.18
Ye, 2014	Medium-duty diesel trucks	1.27
Yao et al., 2015b		1.45
Ye, 2014	Heavy-duty diesel trucks	0.88–3.87
Yao et al., 2015a		1.54–6.61
Yao et al., 2015b		1.86
Cao et al., 2020		0.03–0.26
Yao et al., 2015c	Rural vehicles	5.16–13.46

that typical agricultural machines in Beijing emitted 0.18 Gg of HCs in 2016. Wang et al. (2020) found that tractors and combine harvesters in Beijing emitted 0.33 Gg of HCs in 2017. Guo et al. (2020) found total HC emissions of 86.14 Gg for agricultural machines in the Beijing–Tianjin–Hebei region in 2015. Carbonyl compound emissions from agricultural machines in the same areas estimated from our data accounted for 1.6%–9.9% of total HC emissions for agricultural machines found in the studies mentioned above. This would have been related to the different types of pollutants studied. Dong et al. (2014) estimated that gasoline and diesel vehicles in China emitted 58.4 ± 14.1 and 45.8 ± 28.2 Gg, respectively, of carbonyl compounds in 2011. We found that the amounts of carbonyl compounds emitted by agricultural machines were 32.9% and 42.0% of the amounts of carbonyl compounds emitted by gasoline and diesel vehicles, respectively. The differences in amounts emitted found in the different studies may have been caused by vehicles complying with older emission standards being used in the earlier studies and there being more vehicles than agricultural machines. These results indicate that emissions of carbonyl compound from agricultural machines in China cannot be ignored. The three dominant carbonyl compounds emitted from agricultural machines in China were found to be formaldehyde, acetaldehyde, and acrolein, of which 11.66, 2.96, and 0.77 Gg, respectively, are emitted by agricultural machines in 2019. The areas with high carbonyl compound emissions were concentrated in Northeast China. The provinces Hebei (North China), Zhejiang (East China), Shandong (East China), Heilongjiang (Northeast China), Jiangsu (East China), and Henan (Central China) were found to have the highest carbonyl compound emissions from agricultural machines in China (1.99, 1.89, 1.37, 1.37, 1.08, and 1.00 Gg, respectively). More diesel is used in Hebei (2,001 Gg), Zhejiang (1,905 Gg), Shandong (1,376 Gg), Heilongjiang (1,374 Gg), Jiangsu (1,089 Gg), and Henan (1,001 Gg) than other provinces, and these six provinces together used 45.2% of all diesel used for agricul-

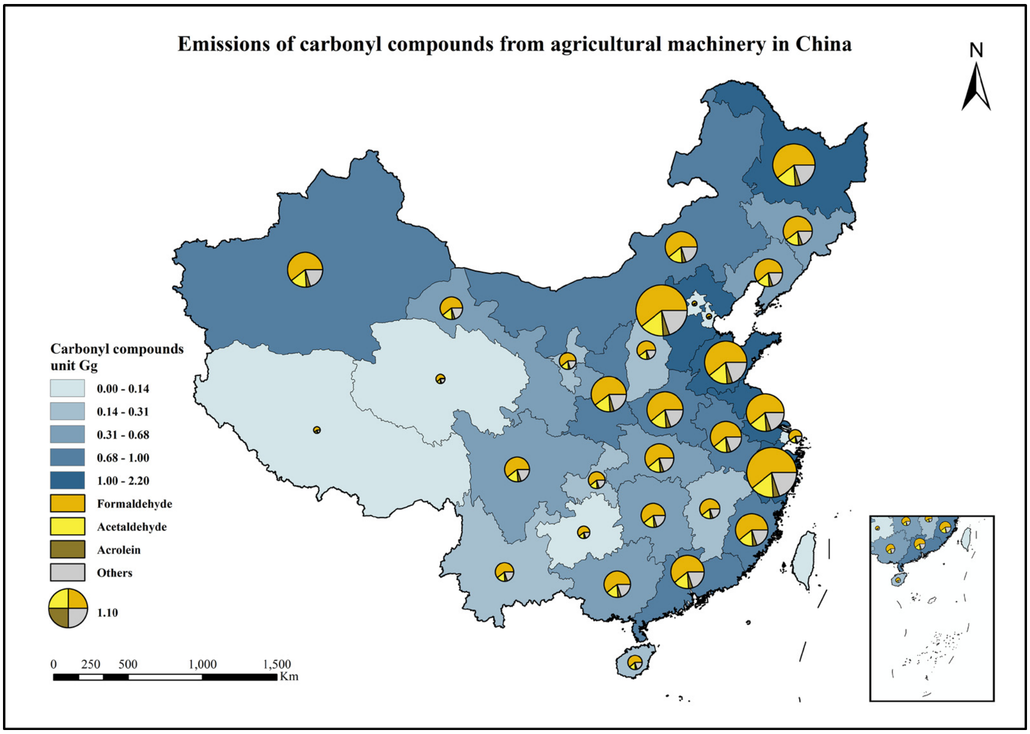

Fig. 7 – Carbonyl compound emissions from agricultural machines in China in 2019.

ture in China in 2019 (NBSC, 2020a). Hebei, Shandong, Heilongjiang, Jiangsu, and Henan are the dominant agricultural provinces in China, with total grain outputs of 37,392, 53,570, 75,030, 37,062, and 66,954 Gg, respectively. These provinces together accounted for 40.7% of grain production in China in 2019. Coastal areas are more polluted than non-coastal areas in China, possibly because coastal areas have more developed economies and use more mechanized tillage processes (NBSC, 2020b).

2.5. *Uncertainty analysis*

Estimating carbonyl compound emissions from agricultural machines inevitably involves several uncertainties. Uncertainties in carbonyl compound emissions were mainly caused by not fully considering the factors affecting emissions. The China I emission standard was applied to agricultural machines for only a short time, and relatively few agricultural machines were produced during that time, and thus no China I agricultural machines were tested. The effects using different types of machines for the tillage processes were not considered. Carbonyl compound emissions from agricultural machines being transported from their storage sites to their workplaces were also ignored.

Uncertainties in total carbonyl compound emissions in different Chinese provinces were mainly caused by uncertainties in activity data and emission factors. Activity data (i.e., agricultural diesel use data) were low-resolution data taken from the relevant statistical yearbooks, and agricultural diesel fuel consumption data for the different emission standards and different tillage processes were temporarily unavailable, and therefore we estimated agricultural diesel fuel consumption using proportional coefficients. A field survey of fuel consumption by agricultural machines during different tillage processes to give data to calculate the proportional coefficients was performed only in Jining City (Shandong Province), and thus there was marked uncertainty in the data. Not testing all types of agricultural machines led to uncertainty in the emission factors. The agricultural machines that were tested are the main types of machines used for tillage processes (only tractors and combine harvesters). Agricultural machines such as diesel-powered irrigation systems and drainage machines were not tested. Factors such as the duration of use, engine type, engine power, and driver habits were not considered. The 95% confidence intervals for the emission factors for sowing using China 0 machines were −93.9% and 48.3%. The 95% confidence intervals for the emission factors for tilling, plowing, harvesting, and returning using China II machines were −200.5% and 66.7%, −267.3% and 72.8%, −3.8% and 3.6%, and −26.5% and 21.0%, respectively. The 95% confidence intervals for the emission factors for China III machines were −24.1% and 19.4% for plowing and −44.5% and 30.8% for harvesting. The coefficients of variation for the emission factors were 0.03–0.68, indicating the large uncertainties in the emission factors. The methods that were used to perform the quantitative analyses are described in Section 1.7. More detailed studies will be required to investigate carbonyl compound emissions from agricultural machines in China in more depth.

3. Conclusions

A total of 20 agricultural machines were tested in Jining (Shandong Province) under real-world tillage processes using a PEMS. Carbonyl compounds emitted by the agricultural machines were analyzed using an off-line 2,4-DNPH high-performance liquid chromatography method, and OFPs for the carbonyl compounds emitted by the agricultural machines were calculated using the MIR method. The results were compared with carbonyl compound emission data and OFPs for other types of vehicles determined in previous studies. Total carbonyl compound emissions from agricultural machines in China were then estimated.

A total of 15 carbonyl compounds were detected, and formaldehyde, acetaldehyde, and acrolein contributed >75% of total carbonyl compound emissions. Agricultural machines were found to emit 8.37–32.29 and 1.79–2.72 times more carbonyl compounds than gasoline and diesel vehicles, respectively, under the various emission standards that have been in place in China. We found that China II agricultural machines emits 51.6% of the carbonyl compounds emitted by other rural vehicles. Larger amounts of carbonyl compounds were found to be emitted by agricultural machines during tillage processes than by other types of vehicles, indicating that carbonyl compound emissions from agricultural machines need to be studied and controlled more than currently. Differences in emission standards and tillage processes affect carbonyl compound emissions and OFPs. Carbonyl compound emission factors were 66.5% lower for China II than China 0 machines and 66.6% lower for China III than China II machines. For China 0 and China II agricultural machines, larger amounts of carbonyl compounds were found to be emitted during sowing than other processes. And for China III agricultural machines, carbonyl compound emission factors were reduced in the order of plowing, tilling, and harvesting. Formaldehyde was found to be the dominant carbonyl compound emitted and to have the highest OFP. Agricultural machines in China were found to have emitted 19.23 Gg of carbonyl compounds in 2019.

Uncertainty in carbonyl compound emissions was found mainly to have been caused by not fully considering the factors that affect emissions. Uncertainty in total carbonyl compound emissions in China were mainly caused by uncertainty in the activity data and emission factors that were used. Carbonyl compound emissions from agricultural machines in China need to be studied in more depth.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.02.031.

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