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Study on characteristics of organic components in condensable particulate matter before and after wet flue gas desulfurization system of coal-fired power plants

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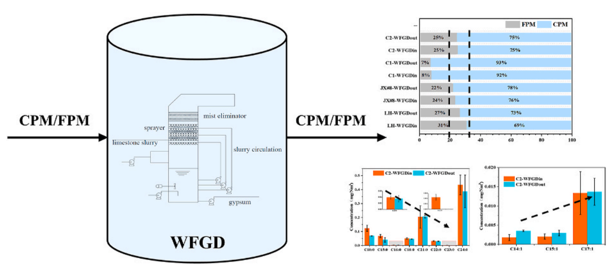
HIGHLIGHTS

- The removal efficiency of FPM2.5 by WFGD of different units varies greatly.
- The removal ability of WFGD to FPM is generally higher than that to CPM.
- The carbon number of all organic compounds in CPM is mostly between 14 and 28.
- The removal rate of phthalate is higher than that of fatty acid methyl esters.
- After WFGD, unsaturated fatty acid methyl ester concentration increased slightly.

GRAPHICAL ABSTRACT



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ABSTRACT

Wet flue gas desulfurization (WFGD) in coal-fired power plants has a great impact on the emission of particulate matter, including filterable particulate matter (FPM) and condensable particulate matter (CPM). In this paper, CPM and FPM in flue gas before and after WFGD in coal-fired power plants were sampled in parallel. FPM was tested according to ISO standard 23210–2009, and CPM was tested according to U.S. EPA Method 202. A method for quantitatively analyzing fatty acid methyl esters in CPM was established, and the removal capacity of fatty acid methyl esters and phthalate esters by WFGD in a typical coal-fired unit was compared. Results show that WFGD has a significant effect on particle size distribution, concentration, and chemical composition. WFGD has a high removal efficiency of inorganic components in CPM, up to 54.74%. CPM contains a variety of organic compounds, including hydrocarbons, esters, siloxanes, halogenated hydrocarbons, and so on. In particular, esters are an important component in CPM, whose concentration tends to decrease after WFGD. Furthermore, a total of 11 fatty acid methyl esters and 5 phthalate esters were detected in CPM before and after WFGD. Noted that fatty

; BMPP, 1,2-Benzenedicarboxylicacid, diisohexyl ester; C1/C2, coal-fired power plant 1/ coal-fired power plant 2; C15:0, Pentadecanoic acid methyl ester; C21:0, Heneicosanoic acid methyl ester; C23:0, Tricosanoic acid methyl ester; CPM, condensable particulate matter; DBEP, 1,2-Benzenedicarboxylicacid,1,2-bis (2-butoxyethyl) ester; DBP, Dibutyl phthalate; DEEP, 1,2-Benzenedicarboxylicacid, 1,2-bis (2-ethoxyethyl) ester; DEHP, Bis (2-ethylhexyl) phthalate; DEP, Diethyl phthalate; DIBP, Diisobutyl phthalate; DMP, Dimethyl phthalate; FPM, filterable particulate matter; $FPM_{2.5}$, filterable particulate matter with particle size less than 2.5 μm; FPM_{10}, filterable particulate matter with particle size less than 10 μm; GC-MS, gas chromatography-mass spectrometer; LLT-ESP, low-low temperature electrostatic precipitator; $PM_{2.5}$, particulate matter with particle size less than 2.5 μm; PM_{10}, particulate matter with particle size less than 10 μm; WFGD, wet flue gas desulfurization.

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acid methyl esters account for 13.38% of CPM, which make a higher contribution to the concentration of particulate matter than phthalate esters, while WFGD has a stronger control effect on the removal of phthalates.

1. Introduction

As people pay attention to the problem of environmental air pollutants ceaselessly, fine particulate matter ($PM_{2.5}$) has gradually come into public sight. $PM_{2.5}$ refers to particulate matter with particle size less than 2.5 μm, which is an important factor causing air pollution, and the main cause of visibility reduction and climate change (Srivastava et al., 2018). Not only that, $PM_{2.5}$ has a negative effect on human health, such as chronic respiratory and cardiovascular disease deterioration, lung function decline, and even premature death (Salvi, 2007; Samoli et al., 2008; Polichetti et al., 2009).

The $PM_{2.5}$ in the atmosphere mainly arises from the traditional soil dust, coal combustion, biomass combustion, automobile exhaust, industrial emission, and other emission sources, as well as the chemical transformation of secondary particulate matter (Yao et al., 2009). As the largest coal consumer in the world, coal-fired power plants are considered the main source of $PM_{2.5}$ pollution in China (Zhene et al., 2016; Korzeniewska et al., 2019). Particulate matter in coal-fired flue gas includes filterable particulate matter (FPM) and condensable particulate matter (CPM). The particle size of CPM is generally 1–2 μm (Pei, 2010; Cano et al., 2017), and about 72% of FPM is less than 2.5 μm (Pei et al., 2016). Therefore, most of the particulate matter emitted by coal-fired power plants belongs to $PM_{2.5}$, and the emission should be strictly controlled. Because the ultra-low emission limit of particulate matter in coal-fired power plants is low, the removal can not only rely on the dust removal system, and the collaborative dust removal capacity of other air pollution control devices needs to be utilized.

Wet flue gas desulfurization (WFGD) system is a necessary air pollution control device for most coal-fired power plants due to its high desulfurization efficiency, reliable operation, and mature technology (Yoo et al., 2002; Yao et al., 2019). When desulfurizer is injected into the desulfurization tower, a large number of physical and chemical reactions occur in the wet desulfurization. Not only more than 90% of SO_2 can be removed (Cordoba, 2015), but also the concentration and composition of FPM and CPM can be significantly affected by WFGD. According to the survey results of Wu et al. (2018), the WFGD of two units decreases FPM concentration in flue gas, while the WFGD of the other two units increases FPM concentration. It is considered that the increase or decrease of FPM concentration depends on the scouring effect and carrying effect of desulfurization slurry. Liu et al. (2018) found that the removal efficiency of FPM by WFGD is 51.1% and the proportion of $FPM_{2.5}$ at the outlet of WFGD increases significantly, whereas without CPM analysis.

CPM has special properties. Unlike FPM, CPM is not in the solid or liquid state in the flue, but in the gaseous or vapor state, which cannot be directly captured by the filter membrane. After being discharged into the atmosphere, CPM will condense into a liquid or solid state. The proportion of CPM in total particulate matter is higher than 55% (Yang et al., 2014, 2018), even up to 90.52% (Li et al., 2019), which is significantly higher than that of FPM. Not only that, studies have shown that the removal efficiency of WFGD on FPM is higher than that on CPM (Yang et al., 2019). Therefore, the ability of WFGD to remove CPM needs to be paid attention to. In order to better explore the methods to control CPM emissions, it is particularly important to study the composition of CPM.

Currently, the research on CPM components is mainly divided into two parts, inorganic components and organic components. Studies have shown that WFGD can effectively remove inorganic ions of CPM, especially SO_4^{2-}, which is usually the main ionic component in CPM (Liang et al., 2020; Yang et al., 2021). In terms of organic components, Wu et al. (2020) found that there are more than half of organic components in CPM, which reveals that attention should be paid to the organic components. Wang et al. (2020) analyzed the CPM samples collected from the flue gas emitted from two coal-fired power plants, and about 100 kinds of organic compounds including alkanes, esters, and amides were determined, with a rich variety. Similar results have been found in the flue gas produced by the one-dimensional coal combustion system designed by Feng et al. (2020). Unfortunately, they lack research on the migration characteristics of specific organics in WFGD. At present, some scholars have studied the content of organic compounds such as n-alkanes (Song et al., 2020; Wu et al., 2021) and polycyclic aromatic hydrocarbons (Li et al., 2017b, 2017c) in CPM. Esters are the main component of CPM produced by coal combustion, and contribute significantly to particulate matter in the atmosphere (Huang et al., 2017; Nespor et al., 2021), but few people have studied it. This means that an effective quantitative method of esters is necessary, which can promote the exploration of more effective methods to reduce the emission concentration of esters in CPM.

At present, the research on CPM emission is still limited, and the synergistic removal ability of WFGD is not clear. This paper discusses the ability of WFGD to remove FPM and CPM of different units and explores the factors affecting the removal ability. The inorganic and organic components of CPM in flue gas before and after WFGD of two coal-fired units are studied. In addition, this study also establishes a method for quantitatively analyzing fatty acid methyl esters in CPM and preliminarily explores the concentration proportion of fatty acid methyl esters in the flue gas of a typical unit. The removal ability of WFGD in a typical unit for two esters is studied. This study fills the research gap of fatty acid methyl esters in CPM and clarifies the characteristics of CPM before and after WFGD.

2. Experimental method

2.1. Subjects

In this study, WFGD of two typical coal-fired power plants (C1 and C2) in China were selected to conduct research. C1 is located in the inland city of Northwest China, while C2 is in the coastal city of Southeast China. During the sampling period, both places were in winter. The general situation of the two power plants is provided in the Supplementary data file (See Table S1). Noted that C2 adopts solar energy and coal complementary power generation mode. During the sampling period, the solar power generation power was high, so the C2 operated at ultra-low load (rated load 300 MW, actual operating load 30 MW). During the test, units kept stable operation with the load remaining unchanged, and the pollution control facilities operated steadily. The sampling sites were arranged at the inlet and outlet of each WFGD. The composition analysis of the coal in the two units is listed in Table S2.

2.2. Sampling system and method

Figure S1 (Wu et al., 2021) gives a diagram of a sampling system for the simultaneous collection of FPM and CPM. The system is composed mainly of sampling probe, Dekati PM_{10} impactor, CPM condensing collector, and flow pump. Dakati PM_{10} impactor is used to collect FPM. The condensing collector for collecting CPM is composed of condensing tube, short stem impinging bottle, and long stem impinging bottle, which are all placed in a water bath. After the CPM in the flue gas enters the condensate collector, it condenses into a liquid phase on the wall of the bottle, thereby being absorbed and collected.

During the sampling process, the sampling tube before the CPM condensate collector and the Dekati PM_{10} impactor are heated to 130 °C, which helps to minimize the influence of moisture in the flue gas. The sampling flow rate is 10 L/min, which meets the requirements of the Dekati PM_{10} impactor. Three parallel samplings were carried out at each sampling point, each sampling time was 90 min, and air leakage was checked during each sampling period.

2.3. Method of sample analysis

2.3.1. Mass concentration of FPM and CPM

Dekati PM_{10} impactor is a selective impactor that can collect particles with different particle sizes. There are three collection films in series and a polyester fiber film in the impactor. The three films collect particles with diameters ≥10 μm, 2.5–10 μm and 1–2.5 μm respectively, and the polyester fiber film collects all particles with diameters ≤1.0 μm. This ensures that $FPM_{2.5}$, FPM_{10}, and total FPM are measured at the same time. After sampling, the mass gain of film and polyester fiber film was recorded.

Deionized water, acetone, and *n*-hexane were used to clean the condenser tube, short stem impinging bottle, long stem impinging bottle, and the connector, respectively, and repeated the operation thrice. The liquid washed with deionized water was collected as the inorganic component of the sample, and the liquid washed with acetone and *n*-hexane was used as the organic component of the sample. The inorganic and organic solutions were respectively evaporated and dried at indoor temperature. Previous studies (Li et al., 2017a) describe the processing steps of CPM in more detail. The weight gain after completely drying was the mass of inorganic and organic components in CPM.

The weight gain of each component was divided by the on-site sampling volume to obtain the mass concentration of the component. Noted that the concentration of the particles was converted to standard concentration under the condition of dry standard 6% oxygen.

2.3.2. Qualitative and quantitative methods of inorganic substances in CPM

Anions (F^-, Cl^-, SO_4^{2-}, NO_3^-) and NH_4^+ were quantitatively determined by ion chromatography (Dionex ICS-2000), and metal elements (Na, K, Mg, Ca, Al) were quantitatively determined by inductively coupled plasma mass spectrometry (ICP-MS, AAS, Thermo iCAP6300, quadrupole mass spectrometer).

2.3.3. Qualitative and quantitative methods of organic compounds in CPM

The organic pollutants in CPM were analyzed qualitatively and quantitatively by gas chromatography-mass spectrometer (GC-MS). The GC-MS instrument was Agilent 6890 N GC/5975B inert XL MSD, and the chromatographic column was HP-5MS (30 m × 0.25 mm × 0.25 mm). High purity nitrogen (99.9995%) is used as carrier gas, and other specific operating conditions are shown in Table S3.

In the preliminary qualitative study of the samples, the components were compared and analyzed to screen the compounds with matching factor greater than 50%. Selective ion scan mode was used for quantitative analysis of phthalate esters and fatty acid methyl esters. Compared with full scan mode, selective ion scan mode can select specific ions with the specific mass-to-charge ratio for specific substances, which has higher sensitivity and selectivity and is conducive to improving the accuracy of the quantitative method. Each substance has its specific qualitative and quantitative ions to distinguish it from other substances. The previous research of our research group has determined the qualitative and quantitative ions of phthalate esters (Song et al., 2020). In this study, the qualitative and quantitative ions of 16 kinds of saturated fatty acid methyl esters and 4 kinds of monounsaturated fatty acid methyl esters were determined by multiple experiments on the standard solution. The abbreviations of these fatty acid methyl esters and their qualitative and quantitative ions are listed in Table S4.

2.3.4. Quality assurance and control

Phthalate esters standard solutions with 6 concentration levels (0.2, 0.4, 1.0, 2.0, 5.0 and 10.0 mg/ml) and fatty acid methyl ester standard solutions with 7 concentration levels (0.2, 0.4, 0.8, 1.6, 2.0, 5.0 and 10.0 mg/ml) were prepared. According to the peak area and concentration, standard curves were established for quantitative analysis. The recoveries of phthalate esters and fatty acid methyl esters were 80.9%–117.7% and 83.3%–118.9%, respectively, confirming the reliability of the method. The correlation coefficients of 15 phthalate esters standard curves are between 0.991950 (DEEP) and 0.999767 (DMP), and the correlation coefficients of 20 fatty acid methyl esters are between 0.991115 (C15:0) and 0.999697 (C23:0), which are all higher than 0.99, meeting the quantitative requirements of the experiment.

3. Results and discussion

3.1. Removal of WFGD on **particulate matter** in different units

The analysis of mass concentrations of FPM and CPM is based on the average value of the consecutive thrice samples at each of the sampling sites. The specific results are listed in Table 1, which also provides the data obtained from researches of two power plants by our research group. Moreover, Table S5 lists the results of other studies for better comparison and discussion. All four power plant in Table 1 have been retrofitted for ultra-low emissions. Through comparison, the removal of WFGD in ultra-low emission units on FPM and CPM is studied.

WFGD in four coal-fired power plants all adopt limestone gypsum desulfurization system, which is the most widely used flue gas desulfurization process in virtue of its high desulfurization performance and low operation cost. In addition to efficiently removing SO_X, WFGD can also synergistically remove particles in the flue gas through the droplet trapping effect of desulfurization slurry during the spray process. As shown in Table 2, WFGD has a strong dust removal capacity including FPM and CPM.

3.1.1. Removal of FPM by WFGD

Except for C2 with ultra-low load operation, the load of LH, JX#8, and C1 decreases in turn, where the FPM concentration decreases as shown in Table 1. This finding may be due to the low coal feed of the unit with small capacity, and the less pulverized coal particles carried in the flue gas of the unit. Noted that the FPM concentration in C2 is higher and the dust removal efficiency of WFGD in C2 is higher. This may due to the ultra-low load operation of C2. The efficiency of boiler in C2 is low, which will cause incomplete combustion and produce more particulate matter. Moreover, the ultra-low load operation of C2 leads to a low flue gas flow rate. Accordingly, the entrainment effect of flue gas on desulfurization slurry is reduced, which is conducive to the removal of FPM by WFGD (Huang et al., 2019). Furthermore, a low-low temperature electrostatic precipitator (LLT-ESP) is installed in C2. LLT-ESP can reduce the temperature of flue gas, and SO_3 in flue gas condenses to form acid mist, which adheres to the dust surface (Xiong et al., 2015; Zhang et al., 2019). Therefore, LLT-ESP can promote the agglomeration of fine particles and the formation of coarse particles, and improve the removal efficiency of downstream WFGD. The above two reasons jointly promote the high removal rate of FPM by WFGD in C2.

As shown in Tables 1 and 2, the concentration of FPM with particle size less than 2.5 μm is generally much than that of FPM with particle size between 2.5 μm and 10 μm and that of FPM with particle size larger than 10 μm. However, the removal efficiency of $FPM_{2.5}$ by WFGD is not entirely satisfactory. WFGD in C1 led to the increase of $FPM_{2.5}$ concentration from 1.21 mg/Nm^3 to 1.24 mg/Nm^3. Similar phenomena have been found in some studies (Xu et al., 2017; Wu et al., 2018; Xia et al., 2018). Xu et al. (2017) found that the mass concentration of FPM with different particle sizes increased in different proportions after WFGD. Xia et al. (2018) found that the increase of FPM with small particle size after WFGD was significantly greater than that reported in the literature. During WFGD, new solid gypsum particles are produced after evaporation and collision due to the desulfurization slurry being

Table 1
Average mass concentrations of FPM and CPM in flue gas (mg/Nm^3).

Units	Operated capacities	Sampling site	FPM			CPM			TPM
			$FPM_{2.5}$	FPM_{10}	FPM	Organic fraction	Inorganic fraction	CPM	
LH (Li et al., 2017a)	1030 MW	inlet	5.60	7.10	7.20	6.60	9.50	16.10	23.30
		outlet	3.10	3.40	3.70	5.90	4.30	10.20	13.90
JX#8 (Song et al., 2020)	1000 MW	inlet	4.51	5.06	5.37	9.25	8.16	17.41	22.78
		outlet	2.69	2.89	3.48	6.24	6.02	12.26	15.74
C1	350 MW	inlet	1.21	3.06	3.64	25.21	17.18	42.39	46.03
		outlet	1.24	1.97	2.43	19.72	10.92	30.64	33.07
C2	30 MW	inlet	3.92	5.01	5.48	8.34	7.96	16.30	21.78
		outlet	2.01	2.78	3.26	5.98	4.01	9.99	13.25

Table 2
CPM and FPM removal efficiency of WFGD in different units (%).

Units	FPM			CPM			TPM
	$FPM_{2.5}$	FPM_{10}	FPM	Organic fraction	Inorganic fraction	CPM	
LH	44.64	52.11	48.61	10.61	54.74	36.65	40.34
JX#8	40.35	42.89	35.20	32.54	26.23	29.58	30.90
C1	−2.48	35.62	33.24	21.77	36.44	27.72	28.16
C2	48.72	44.51	40.51	28.29	49.62	38.71	39.16

carried by flue gas. The FPM concentration at the inlet of WFGD in C1 is very low, which limits the scouring effect of desulfurization slurry and the removal capacity of WFGD. Accordingly, the concentration of newly formed $FPM_{2.5}$ by carrying particles in the slurry is higher than that of removal in WFGD, resulting in the increase of $FPM_{2.5}$ concentration. Nevertheless, the removal efficiency of WFGD in C1 to the total FPM is satisfactory and can make a certain contribution to the removal of FPM and CPM. Many experimental studies have found that there are a large number of particles with particle size larger than 10 μm in the desulfurization slurry (Wang et al., 2020), which will be carried by the flue gas in the contact process. This explains the phenomenon that the removal rate of total FPM by WFGD of all units in this study is generally lower than that of FPM_{10}. Through field experiments, this study confirmed that WFGD in ultra-low emission units has a lower removal efficiency on particles with a particle size greater than 10 μm.

3.1.2. Removal of CPM by WFGD

As shown in Fig. 1(a), except for C1, the ratio of CPM to FPM of other units is between 2.23 and 3.52. C1 was tested in the winter of Northwest China, and the ambient temperature was very low, causing the low temperature of condensate water used to cool CPM. Consequently, more CPM were generated and the CPM proportion of C1 was higher than that of other units. Accordingly, it can be inferred that the concentration of CPM and FPM may be related to some extent. As the current coal-fired power plants only have real-time data of FPM, it is expected that the approximate concentration of CPM can be estimated from the concentration of FPM. Certainly, more experiments and continuous exploration are needed to confirm this conclusion. Although the concentration of CPM is much higher than that of FPM at the inlet of WFGD, the removal efficiency of CPM is slightly lower than that of FPM by WFGD, which is caused by the special properties of CPM. The temperature in WFGD is low, and part of CPM condenses to form FPM. By simulating the formation of CPM in WFGD, Zheng et al. (2020) found that the particle size of CPM in WFGD is very small, all less than 2.5 μm. As can be seen from Table 2, regardless for $FPM_{2.5}$ or CPM, the removal efficiency of WFGD in C2 is the highest among the four units, followed by the WFGD in LH, JX#8, and finally the WFGD in C1. Therefore, it is speculated that the removal efficiency of $FPM_{2.5}$ by WFGD also affects the removal efficiency of CPM to a certain extent. This provides a new perspective for WFGD to remove CPM, that is, to improve the removal efficiency of WFGD to CPM by improving the removal rate of WFGD to $FPM_{2.5}$.

The proportions of organic and inorganic components in CPM at inlet and outlet of WFGD are shown in Fig. 1(b). The concentration of organic components is generally slightly higher than that of inorganic components from Fig. 1(b). Besides, the proportion of organic components at the outlet of WFGD is generally higher than that at the inlet, which indicates that the removal capacity of organic matter by WFGD is significantly lower than that of inorganic matter. The low removal rate of

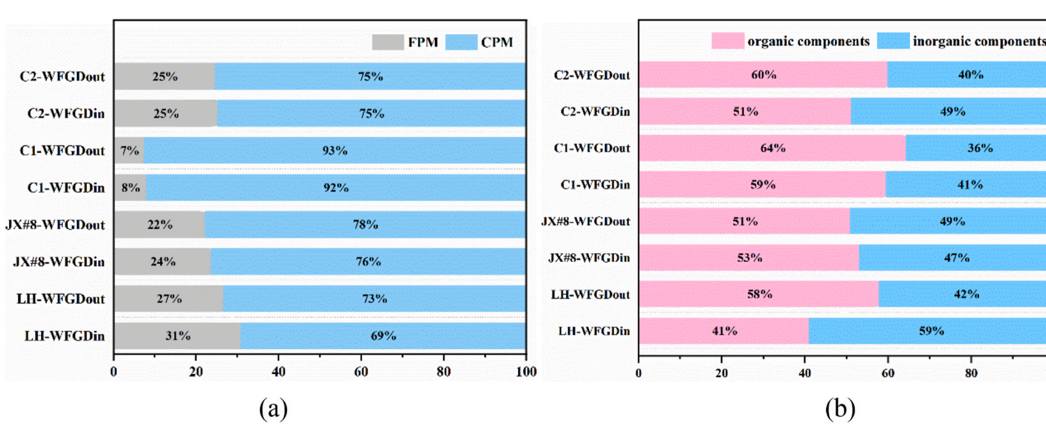


Fig. 1. Proportions of different PM at inlet and outlet of WFGD. (a) CPM and FPM (b) organic and inorganic components in CPM. Note: C1-WFGD, WFGD in C1; C1-WFGDin, inlet of WFGD in C1; C1-WFGDout, outlet of WFGD in C1.

organic matter is probably due to the fact that most organic matter is insoluble in water, compared with inorganic matter, and difficult to be removed by entrainment of the desulfurization slurry.

3.2. Composition analysis of CPM in flue gas before and after WFGD

Evidently, the concentration of CPM is much higher than that of FPM from Fig. 1(a), so it is necessary to analyze the specific components in CPM in detail. However, the chemical profiles reported previously from the coal-fired plants are mainly focused on FPM, and those of CPM has not been sufficiently investigated. Therefore, the components of CPM in flue gas before and after WFGD are analyzed in detail below.

3.2.1. Inorganic components in CPM

The concentration of inorganic ions in CPM is piled in Fig. 2. In the determination of anions, SO_4^{2-} were measured in C1 and SO_4^{2-}, NO_3^-, Cl^- and F^- were measured in C2. Almost all the inorganic ions have a downward trend, which is consistent with the variation of total inorganic ions. SO_4^{2-} is the most concentrated ion in anions, which is related to the sulfur content in raw coal. Besides, the decrease of SO_4^{2-} concentration is attributed to the high removal rate of sulfuric acid mist by WFGD. Ca^{2+} is the highest concentration of cations, and the removal of WFGD on Ca^{2+} is not obvious, even the concentration of Ca^{2+} after C2-WFGD increases, owing to the flue gas carrying the desulfurization slurry.

The water-soluble ions of CPM are closely related to the gaseous precursors. Gaseous precursors include HCl, HF, NH_3, SO_2, and SO_3. According to the definition of CPM, it is gaseous in the flue and dissolved in water after being discharged into the atmosphere to form Cl^-, F^-, NH_4^+, SO_3^{2-} and SO_4^{2-}. In addition to the high removal efficiency of SO_4^{2-}, WFGD also has a strong synergistic removal ability for NH_4^+. NH_3 is the precursor of CPM, which can easily react with limestone in desulfurization slurry and be absorbed by droplets in the desulfurization tower, and the concentration of NH_4^+ also decreases significantly. Noted that the concentration of Cl^- and F^- increased slightly from Fig. 2(b). Studies have found that the concentration of Cl^- and F^- ions in the water-soluble ions in the desulfurization slurry is very high (Ruan et al., 2019). It is inferred that the addition of desulfurization slurry caused the increase of Cl^- and F^- in CPM. Besides, a large amount of H_2SO_4 is produced in WFGD, which may leading to the reaction of strong acid replacing weak acid, such as $NH_4Cl + H_2SO_4 \rightarrow NH_4HSO_4 + HCl$. Hence, the emission concentration of HCl, the gas precursor of Cl^-, increases, so that Cl^- increases in CPM.

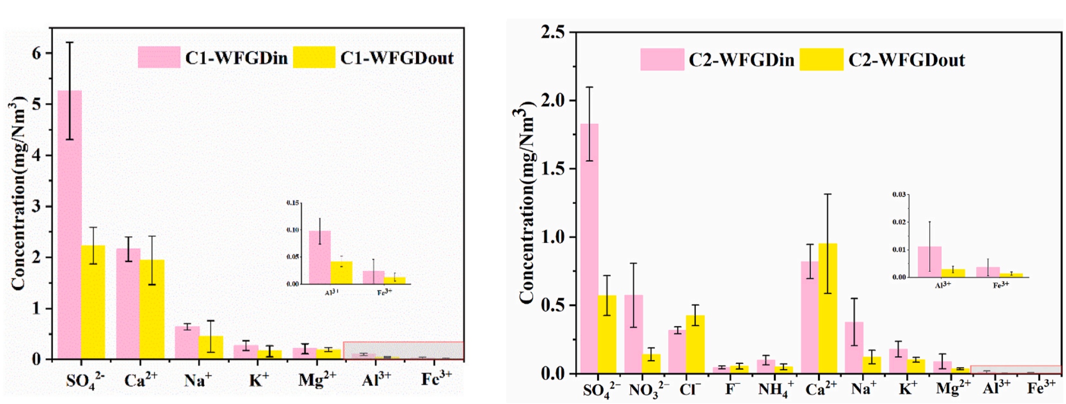
3.2.2. Organic components in CPM

As can be seen in Fig. 1(b), the proportion of organic components in CPM is higher than 50%, except for the organic components at inlet of WFGD in LH. The low proportion of organic components (41%) at the inlet of LH-WFGD can be attributed to the good combustion conditions of the LH coal-fired boiler, and the coal combustion is very sufficient. Numerous studies have confirmed that the organic matter concentration in CPM of the final flue gas discharged from the power plant is higher than that of inorganic matter (Yang et al., 2019; Wang et al., 2020). By comparing the composition of CPM in four groups of flue gas at inlet and outlet of WFGD, this study indicates that organic pollutants are not only the main component of flue gas discharged from the chimney, but also the main component of CPM in flue gas before and after WFGD. However, the current research on CPM organic matter mostly stays at the level of total organic matter concentration. Therefore, it is necessary to enrich the chemical characteristics of CPM in power plant flue gas and make an in-depth exploration on how WFGD controls CPM emission.

In the preliminary qualitative study of organic samples in CPM, the components were compared and analyzed to screen the compounds with matching factor greater than 50%. The organic components in CPM at inlet of C1-WFGD are listed in Table S6. A total of 50 organic compounds were detected, including hydrocarbons, esters, siloxanes, halogenated hydrocarbons, phenols and alcohols. Among them, saturated hydrocarbons can cause disorders in the nervous system, stimulate the respiratory system, and damage the skin, while unsaturated hydrocarbons have strong irritation and anesthesia (Yassaa et al., 2001). Esters may be toxic to kidney and testis (Gao et al., 2019). Siloxane can damage liver and fertility, and even show potential carcinogenic effects (Fromme et al., 2015). Phenolic organic pollutants can cause protein denaturation, cell poisoning or death (Taamalli et al., 2012). This suggests that the CPM discharged by the power plant contains a large amount of toxic and hazardous organic matter, which needs widespread attention.

CPM in coal-fired flue gas contains a variety of organic compounds, which have a wide range of molecular weight and functional groups, and have different physical and chemical properties such as volatility and solubility. Combined with the organic components of CPM in the flue gas of C1-WFGD (Table S6), the results suggest that the carbon number of all organic matters is mostly between 14 and 28. Studies have suggested that the number of carbon atoms of intermediate volatile organic compounds (IVOCS) is between 13 and 19, and that of semi volatile organic compounds (SVOCs) is between 20 and 26 (Gentner et al., 2017). Consequently, the results imply that the organic compounds in CPM are intermediate volatile organic compounds or semi volatile organic compounds, which exist in the form of gas or particle phase, and even can exist in two phases at the same time.

Fig. 3 lists the peak area ratio of organic components, which can represent the concentration ratio to a certain extent. Esters, hydrocarbons and siloxanes are the main components of CPM organic components as shown in Fig. 3. Furthermore, studies have confirmed that esters are important components of organic components of CPM (Li et al.,



(a) (b)

Fig. 2. Concentration of inorganic ions in CPM at inlet and outlet of WFGD in different units. (a): C1 (b): C2

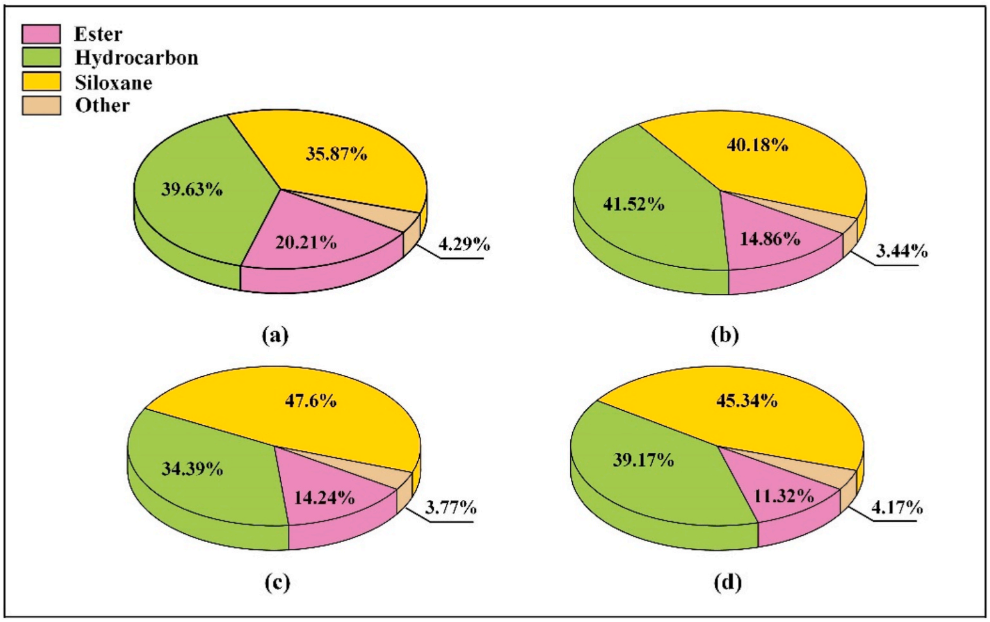


Fig. 3. Proportion of peak area of organic components in CPM at different sampling point (%). (a) C1-WFGDin (b) C1-WFGDout (c) C2-WFGDin (d) C2-WFGDout.

2019; Yang et al., 2021). The results show that the ratio of peak area of esters decreases obviously after WFGD from Fig. 3. It is speculated that WFGD can remove esters organics, which may due to the low temperature of WFGD, promoting the condensation and dissolution of some organics. Meanwhile, on account of the particularity of esters, they can react with water, some of which are converted into other organic compounds after washing by desulfurization slurry and the concentration is significantly reduced. From Fig. 3, as can be seen, the peak area ratio of hydrocarbons increases. This requires us to quantify more organics in follow-up studies to explore whether there are organics with increased concentration and explore their removal methods.

3.3. Accurate quantitative analysis of two esters in CPM before and after WFGD of a typical unit

According to the preliminary qualitative analysis, esters are an important part of organic components of CPM. A variety of esters were detected, such as diisobutyl phthalate, methyl heneicosanoate, methyl stearate and octadecyl acetate, which can be mainly divided into alkane esters and aromatic esters. In this study, the typical esters, fatty acid methyl esters and phthalate esters, were selected respectively for accurate quantitative study to explore the removal ability of WFGD in C2.

3.3.1. Fatty acid methyl ester

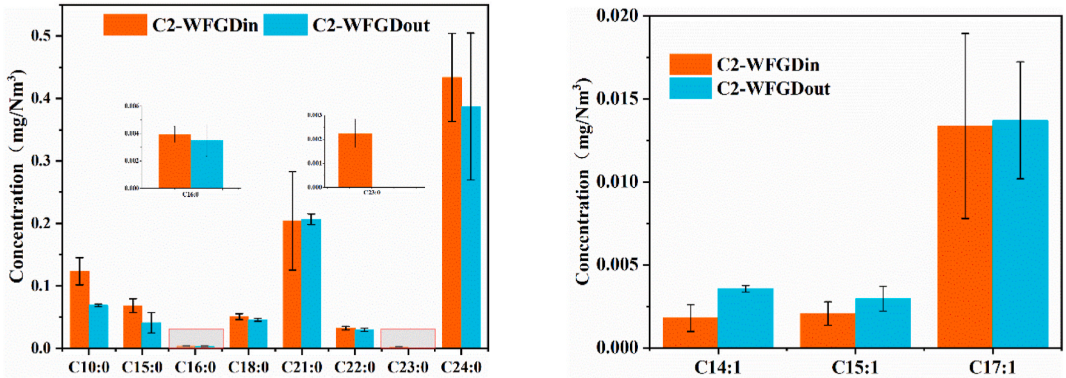
According to the qualitative results in the previous chapter, alkane esters, such as 2,2,4-trimethyl-1, 3-pentanediol diisobutyrate, octadecyl acetate, methyl octadecanoate and methyl stearate were detected, among which, there are many kinds of fatty acid methyl esters in CPM. Fatty acid methyl esters were found to exist in atmospheric particulate matter (Nespor et al., 2021), causing pollution to air quality, but there was no study on their distribution in CPM.

8 saturated fatty acid methyl esters and 3 monounsaturated fatty acid methyl esters were detected at inlet and outlet of C2-WFGD, and the total concentration decreased from 0.94 mg/Nm^3 to 0.80 mg/Nm^3. Some fatty acid methyl esters with lower carbon numbers were not detected (Methyl butyrate, Methyl caproate and Methyl octylate), which may result from the high volatility of fatty acid methyl esters with lower carbon numbers. This study show that the concentration of fatty acid methyl esters is relatively high, which account for 11.27% and 13.38% of the total organic matter, respectively. Existing data showed the proportion of n-alkanes and phthalate esters in CPM organic matter is less than 15%, and the proportion of polycyclic aromatic hydrocarbons in CPM organic matter is even less than 1% (Song et al., 2020; Li et al., 2021). Therefore, it can be known that fatty acid methyl esters are one of the main components of CPM organic components in flue gas. This study has a great advance in the exploration of the components of CPM.

Fig. 4 gives an image of the changes in the concentration of two types of fatty acid methyl esters after flue gas passes through WFGD. On the whole, WFGD can effectively remove saturated fatty acid methyl esters. Fig. 4(a) shows that the concentration of fatty acid methyl esters with a lower or higher carbon number has a larger decrease, while the concentration of fatty acid methyl esters with a middle carbon number has a smaller change, and even the concentration of C21:0 (Methyl heneicosanoate) slightly increases. This phenomenon may be from that the solubility of fatty acid methyl esters with lower carbon number is higher than that of fatty acid methyl esters with higher carbon number. The fatty acid methyl esters with lower carbon can be partially dissolved in water, and then enter desulfurization wastewater or be removed by demister. While the decrease of the concentration of fatty acid methyl esters with higher carbon number might be attributed to the high boiling point. Due to the low temperature in WFGD, the organic matter with high boiling point can be easily converted into liquid phase and removed. Different from the conclusion of saturated fatty acids, the concentration of methyl monounsaturated fatty acid methyl esters showed a slightly increasing trend, as shown in Fig. 4(b), the reason for its formation is not yet clear. Nevertheless, compared with saturated fatty acid methyl ester, its content is too low to affect the concentration of total organic matter.

3.3.2. Phthalate esters

The preliminary qualitative aromatic esters in this study include diisobutyl phthalate, bis (2-ethylhexyl) phthalate and phthalate-1-butyl ester-2-isobutyl ester etc., all belong to phthalate esters, which can destroy the immune system and affect gene expression and cell function, increase the risk of testicular cancer and infertility and long-term exposure will increase the risk of breast cancer in women (Mahood et al., 2005). In this study, phthalate esters were selected as typical aromatic esters for quantitative research. Compared with fatty acid methyl esters, fewer phthalate esters can be detected in the samples. Among the CPM components in the flue gas at inlet and outlet of C2-WFGD, only 5



(a) (b)

Fig. 4. Concentration of fatty acid methyl esters at inlet and outlet of C2-WFGD: (a) saturated fatty acid methyl esters and (b) monounsaturated fatty acid methyl esters.

of 15 phthalates were detected in this study, respectively DEP, DBP, BMPP, DBEP and DEHP, which are not exactly consistent with the previous studies. Wu et al. (2021) illustrated that five kinds of phthalates (DMP, DIBP, DBP, DEEP and DEHP) were found at the inlet and outlet of WFGD, and the concentration of phthalate esters decreased by 55.68% ~ 58.51%. Similar to results of Wu et al. (2021), the results of this experiment also show that DBP is the most abundant of phthalate. DBP and DEHP are all the blacklist of priority pollutants in China, and need further study to control their emissions.

Fig. 5 shows the concentration changes of five phthalate esters in CPM at inlet and outlet of C2-WFGD. The result indicates that the content of phthalate esters in CPM is lower than that of fatty acid methyl esters, and the concentrations at inlet and outlet of C2-WFGD are 0.39 mg/Nm^3 and 0.23 mg/Nm^3 respectively, accounting for only 4.68% and 3.85% of organic components. The concentrations of five phthalate esters decreased to varying degrees after the flue gas passes through WFGD, especially DBP, which decreased by 72.54%. CPM contains many organic compounds with various functional groups, such as carboxyl, alcohol hydroxyl, phenol hydroxyl and so on. These organic compounds have high reaction activity and can adsorb phthalates such as DBP through hydrogen bonding, so as to reduce the concentration of phthalate esters in CPM (Song et al., 2014). A large number of studies have found that phthalate esters can be physically adsorbed by activated carbon, porous carbon and graphene (Zhou et al., 2016; Hao et al., 2019). Particle matter with large surface area and adsorption capacity in flue gas is a lot, which can adsorb phthalate esters in FPM and be removed in WFGD. At the inlet of WFGD, DBP concentration is the highest, which is easier to be adsorbed and removed. This may account for the significant decrease in its concentration. In summary, WFGD can indeed effectively remove esters, and the removal ability of phthalate esters (aromatic esters) is stronger than that of fatty acid methyl esters (alkane esters).

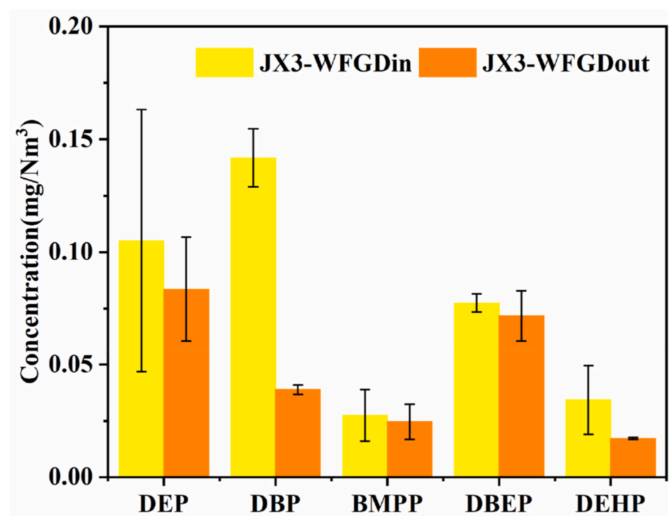


Fig. 5. Concentration of phthalate esters at inlet and outlet of C2-WFGD.

4. Conclusions

In this study, the effects of WFGD system on the concentration of FPM and CPM in different coal-fired power plants were compared. The organic and inorganic components of CPM at inlet and outlet of WFGD in two coal-fired units were studied respectively. Besides, the two typical esters of CPM in flue gas before and after WFGD of a typical coal-fired power plant were quantitatively analyzed. Detailed conclusions are listed below: (1) The removal efficiency of $FPM_{2.5}$ by WFGD of different units varies greatly, from −2.48% to 48.72%. WFGD in ultra-low emission units has low removal efficiency for particles with particle size larger than 10 μm, which has low concentration. (2) The removal ability of WFGD to FPM is higher than that to CPM. The removal ability of WFGD to CPM organic matter is lower than that to inorganic matter. (3) SO_4^{2-} and Ca^{2+} are the most concentrated anions and cations in the inorganic components respectively. Except Ca^{2+}, Cl^- and F^-, other ions all show a downward trend, which indicates WFGD may increase the emission of inorganic ions contained in the desulfurization slurry. (4) CPM contains a variety of organic compounds, and the carbon number of all organic compounds is mostly between 14 and 28. Esters are important components of CPM, and the peak area account for 11.32%–20.21%. (5) Fatty acid methyl esters account for 13.38% of CPM, which make a higher contribution to the concentration of particulate matter than phthalate esters. WFGD has a certain removal effect on the two typical esters, and the removal efficiency of phthalate esters is 38.86%, which was higher than that of fatty acid methyl esters.

Credit author statement

Siqi Liu: Conceptualization, Data curation and analysis, Writing Original draft. **Yujia Wu:** Reviewing and Editing. **Zhenyao Xu:** Investigation. **Shengyong Lu:** Methodology. **Xiaodong Li:** Conceptualization, Supervision.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.133668.

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