Chemical profiles of PM emitted from the iron and steel industry in Northern China

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Abstract

Source-level sampling methods were adopted in this study to sample six iron and steel plants referring four main manufacturing processes, with over 150 samples collected and measured in this study, the latest data for iron and steel industry in China has been demonstrated. The emission factors of CO₂, CO, SO₂, NO_x, TSP, PM_{2.5} and PM₁₀ were calculated, and the majority of pollutants were emitted from the sintering process. The virtual impactor divided the PM sample into three size fractions for chemical profiles and the profiles indicate that SO₄²⁻, NH₄⁺ and OC distribute more into fine particles. The elements in PM from the sintering, pelletizing, puddling

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and steelmaking processes were measured and compared using the coefficient of divergence. The divergence between PM_{2.5} and PM₁₀ for the same process is not obvious, with CD values ranging from 0.1697 to 0.2578. PM_{2.5} profiles of four process were notably different from one another, with CD values ranging from 0.4802 to 0.7500. More efforts are needed to update the PM profiles in China. PAHs in PM were investigated, and most of the PAHs in PM are from the sintering process. The total PAH concentration in PM_{2.5} from the sintering process is 73.28±1.45 µg/m³ with a BaPE value calculated at 9.92 µg/m³.

Keywords: *Iron and steel industry, PM source profiles, Emission factors, PAHs*

1. Introduction

Chemical source profiles of particle matter (PM) are the foundation of atmospheric PM source apportionment, and the accuracy of the source apportionment is mainly tied to the source data input (Raman et al. 2007, Liu et al. 2014, Zhang et al. 2014). Unlike the SPECIATE database established by the US Environmental Protection Agency (Simon et al. 2010), the local PM source profile database of China is still unformed, limiting the effective control of pollutant emissions.

The PM profiles of regional fugitive dust (Ho et al. 2003, Xu et al. 2012, Kong et al. 2014, Chen et al. 2016, Elena et al. 2016), vehicles (Li et al. 2013, Stroe et al. 2014, Wu et al. 2015, Sahanavin 2016) and coal and bio-fuel combustion (Ciuta 2012, Ma et al. 2015, Li et al. 2016) have already been extensively investigated in China, while local industrial source information has seldom been reported. According to the statistical data reported by the Ministry of Environmental Protection of China, over 85%

of SO₂, 65% of NO_x and 80% of PM were emitted from the industrial sources in 2014, the total industrial PM emission reached 14.561 million ton, making industrial source pollution control extremely critical to improve China's air quality.

Thermal power plant is the biggest industrial PM emission source in China with 2.355 million ton PM emitted in 2014, some studies related to the emission inventory (Ma et al. 2016), emission profile (Ai et al. 2011, Kong et al. 2013) and control technology (Zhao et al. 2014) have already been performed. The dilution sampling method has been adopted, with the basic consistent conclusion of that PM_{2.5} emissions from coal-fired plants include Al, Ca, Fe, K, SO₄²⁻, NH₄⁺ and organic carbon (OC), while the absolute concentrations of these elements are influenced by the coal species and combustion conditions (Nielsen et al. 2002, Yi et al. 2006).

Apart from the thermal power plant, iron and steel manufacturing plants are the second biggest industrial PM emission source in China, the traditional long process of iron and steel plants has caused huge quantities of energy consumption and significant pollutants emission, with 1.02 million ton PM emitted in 2014. As for the PM profiles of iron and steel plants, so far there were no more than ten iron and steel plants been reported by the literature (Yang et al. 2002, Kong et al. 2011, Yang 2015, Wang et al. 2016), one reason may limited by the sampling method, another may caused by the complex processes of iron and steel manufacturing, the accurate source profiles is more difficult for iron and steel industry. The profiles for iron and steel plants are quite different because of the different industrial processes and manufacturing regions; SO₄²⁻, Cl⁻, K, OC and Ca are the main contributors at the sintering plant, while Fe and

Zn dominate PM_{2.5} emissions from the smelting furnace plant (Amodio et al. 2013, Zheng et al. 2013). These significant discrepancies in chemical species are closely linked to many factors, meaning that the chemical profiles of the iron and steel industry are far from completion.

So far the published profiles of iron and steel plants in China are from 2009 to 2015, almost all the samples were collected after de-dusting facilities, only one profile in Shanghai (Zheng et al. 2013) takes the desulfurization into consideration. Sintering is the main pollutants emission source in iron and steel plants, the national emission standard for sintering flue gas (GB 28662-2012) has been published in 2012 and regulated the SO₂ at 200 mg/m³ since 2015, also the total PM in iron and steel plant has been requested to be under 50 mg/m³, so with the establishment of the matching desulfurization and de-dusting facilities, PM profiles emitted from sintering machine to the air need to be updated to reflect the real emission status, this is one important point should be mentioned.

Considering the urgency of establishing the latest PM chemical profiles for the iron and steel industry, six iron and steel plants were all chosen with desulfurization and de-dusting facilities, the desulfurization methods include both the wet flue gas desulfurization and the semi-dry flue gas desulfurization, de-dusting methods include the electrostatic precipitator and the bag filter, most of these pollutants control facilities are installed after 2012. The locations of these plants were in Jing-Jin-Ji area of northern China, which possesses a quarter of the national iron and steel production, the steel annual production capacity ranges from 100 to 800 million ton, covering the

typical local iron and steel industry. The sampling period is lasted from March to November 2015, all the sampling work has been proceeded under fine days (10~28°C), without rainy or snowy weather to avoid the sample pollution, the sampling sites are closely related to the latest pollutants control facilities, so the data in manuscript can reflect the real emission profiles at present, which is much more precious for developing the iron and steel industry profiles in China. Source-level sampling method were adopted to reflect real emission conditions, and the primary emission processes were comprehensively compared. The aim of this research is to focus on establishing and updating the chemical profiles of the iron and steel industry in northern China. Polycyclic aromatic hydrocarbons (PAHs) were also characterized in this work, providing the latest information for the PM source.

2. Methodology

2.1 Sampling

2.1.1 Sampling sites description

Six typical iron and steel plants in northern China were chosen based on production scale, location, production process, pollution control facilities and raw materials. The iron production capacity of these six plants are all above 100 million tons per year where those plants are located in northern China and use the traditional long production process. The details of the plants are shown in Table 1.

2.1.2 Flue gas parameters

The concentrations of flue gas components were detected using a flue gas analyser (Testo350, Germany). The resolution of O₂ and CO₂ measurements are 0.01

Vol.%; CO is 1ppm; and NO_x and SO₂ are 0.1 ppm. Flue gas temperature, flow rate and total suspended particulate (TSP) concentrations were determined using an automatic dust sampling instrument (3012H, Qingdao Laoying Co. China).

2.1.3 Particulate matter sampling description

The TSP was sampled by the automatic dust sampling instrument, the sampling flow rate was 10-60 L/min, and TSP concentrations were collected using a quartz filter cartridge (φ28×70 mm, Qingdao Laoying Co. China) and weighed on a sensitive microbalance (MS105DU, METTLER) with a sensitivity of ±0.01 mg.

A two stage virtual impactor was adopted to collect PM₁₀/PM_{2.5} from flue gas, which was self-developed by Tsinghua University (Jiang et al. 2014). The PM has been sieved into three levels through the virtual impactor, including PM_{2.5} (aerodynamic diameter less than 2.5 μm), PM₁₀ (aerodynamic diameter less than 10 μm) and PM_{>10} (aerodynamic diameter larger than 10 μm). The virtual impactor showed highly satisfactory performance for PM_{2.5} mass concentrations and separation efficiency within the investigated range of mass concentrations and ambient conditions (Wada et al. 2016). The collection efficiency curve meets the requirement of ISO 13271, 2012 for virtual impactors. The diameter of this cylindrical virtual impactor is 74 mm, smaller than the diameter of the sampling port in most industrial sources in China. Taking the sampling sites of the sintering process as an example: the gas flow is stable, and the sampling site was chosen at the end of the pollution control facility, reflecting the PM actually emitted to the ambient environment (Figure 1).

2.1.4 Filters pre-treatment and storage

Three parallel samples were taken at each sampling site. The first and third parallel samples were collected using quartz-fibre filters ($\phi 37$ mm, Pall Corp. USA); the second parallel sample was collected by using Teflon-membrane filters ($\phi 37$ mm, Pall Corp. USA). Blanks filters were treated in the same manner as the PM samples.

All the quartz fibre filters were calcined ($450\text{ }^{\circ}\text{C}$ for 2 h) to remove organic compounds prior to sampling. Calcined quartz fibre filters and Teflon-membrane filters were equilibrated in a constant temperature (25°C) and humidity ($\text{RH}=50\%$) system for 48 h before gravimetric analysis. Filters were weighed both before and after sampling using a microbalance and were stored at $-4\text{ }^{\circ}\text{C}$ after weighing.

2.2 Sample analysis and quality control

2.2.1 Elemental analysis

Teflon filters were detected by X-ray fluorescence (RIX3000, Rigaku Corp. Japan) for elemental analysis, including 9 crustal elements (Si, Ti, Al, Mn, Mg, Ca, Fe, K, Na) and 19 other trace elements (Cl, P, S, Sc, V, Cr, Co, Ni, Cu, Zn, As, Se, Br, Sr, Cd, Ba, Pd, Sn, Sb).

2.2.2 Ion analysis

A quarter of each quartz filter was cut into a vessel then extracted three times with 5 ml of ultrapure water using ultra-sonication and mechanical shaking in an ultrasonic cleaner at a frequency of 40 kHz for 30 min. The solution was then drawn into a syringe, filtered and injected into an ion chromatograph (DX-600, Dionex, USA) with a flow rate of 1.0 ml/min.

2.2.3 Carbon analysis

Another quarter of each quartz filter was used for OC and EC analyses using a thermal/optical carbon analyser (DRI Model2001A, Atmoslytic, USA); the minimum detection limit for OC is $0.82 \mu\text{gC}/\text{cm}^2$, and EC is $0.2\mu\text{gC}/\text{cm}^2$.

2.2.4 PAH analysis

For PAH analysis, gas chromatography (7890A, Agilent, USA) coupled to mass spectrometry (JMS-Q1000GC) (GC-MS) was used. The chromatographic column is a capillary column with a DB-5MS (30 m $\times$ 0.25 mm $\times$ 0.25 μm), and the purity of the helium gas was 99.999% or higher. The filters were extracted via soxhlet extraction with n-hexane, dichloromethane and a PAHs purify solution. The extracting solution was concentrated using a rotary evaporator at 45 °C and purified with a silica gel clean-up technique and then re-concentrated by rotary evaporation. Finally, the extracts were condensed to exactly 0.5 mL under eluting liquid nitrogen. The purified extracts were transferred into labelled sample bottles using a pipetter and stored in a refrigerator until analysis.

2.2.5 Quality assurance (QA) and quality control (QC)

Sampling sites were chosen to be without fugitive dust or other pollution sources. Each filter was weighed 3 times before and after sampling, and the filter was packed with aluminium-foil and stored in a plastic container. The sampling impactor was cleaned by ethanol each time before sampling. Surgical masks and disposable gloves were worn when dealing with the filter to avoid any contamination of the samples.

For the chemical analysis, blank samples comprised 10% of the total test samples, and the detect value of the blank sample should be an order of magnitude lower than

the detection limit. The relative standard deviation (RSD) for the ions were 0.085% for NH_4^+ , 0.88% for NO_3^- and 1.718% for SO_4^{2-} . For carbon analysis, a saccharose standard solution ($3.104 \mu\text{gC}/\mu\text{L}$) was used for calibration. One in every ten samples was repeated, and the precision was less than 3%.

3. Results and Discussion

3.1 Pollutant emissions in the iron and steel industry

The description of the sampling sites and pollutant emission concentrations are provided in Table 1. Four different desulfurization technologies were chosen for the sintering process. The SO_2 concentration after desulfurization varied between 94.29 and $277.14 \text{ mg}/\text{m}^3$. Two plants exceeded the national emission standard of $200 \text{ mg}/\text{m}^3$ for SO_2 . There are no special denitration facilities for sintering gas, and almost all of these plants meet the national standard of $300 \text{ mg}/\text{m}^3$ for NO_x , except for plant A, which was $12 \text{ mg}/\text{m}^3$ over the standard. The national standard for TSP is $30 \text{ mg}/\text{m}^3$, where only plant A and plant E meet this requirement. The other plants need further efforts to avoid excessive emissions. The pelletizing process was only investigated in plant B, and the high concentrations of SO_2 ($520 \text{ mg}/\text{m}^3$) found at this location are because of a desulfurization facility that is currently under construction. As for puddling and steelmaking processes, all the sampling sites are located after the secondary dedusting, and the blast gas was recycled after the primary dedusting.

Based on the emission parameters in Table 1 and the production data for these plants, the emission factors for each process can be calculated with the following equation, and the results are shown in Table 2.

$$k_i = \frac{C_i \times Q \times 273.15}{P_j \times (273.15 + T) \times 10^6} \quad (1)$$

where k_i is the pollutant emission factor in kg/t; C_i is the average emitted pollutant concentration in mg/m³; i indicates the type of pollutant; Q is the flue gas volume flow in m³/h; T is the flue gas temperature in °C; P_j is the average amount of product per unit time in t/h; and j indicates different production processes.

As shown in Table 2, the average emission factors for sintering, puddling and steelmaking processes were estimated. Similar to pervious research (Wu et al. 2015, Wang et al. 2016), the majority of acidic gaseous pollutants were discharged from the sintering process, while the calculated SO₂ emission factor of this research at 0.62±0.004 kg/t is much less than other data obtained before 2010, as compared in table 2, greatly can be caused by the desulfurization facilities, as for NO_x emission factors, the data at 0.62±0.003 kg/t is quite the same with others, meaning the NO_x emission inventory is very stable under the no additional request for reduction, TSP and PM emission factors in this research are quite lower than others, which could also been contributed to de-dusting facilities, the direct CO₂ emission factor for sintering flue gas is 280.6±65.5 kg/t, which is quite close to the value (220~304 kg/t) calculated from the raw material consumption (Xu et al. 2016). Analogously, the TSP and PM emission factors for puddling and steelmaking process in this research are also lower than others due to the de-dusting facilities, these changes is typically obvious for these six plants selected are all under the strictest emission standards.

Sintering process is still the focus of pollution control for the whole manufacturing process. For the particulate matter, the TSP emission factor of the

sintering process is 7 times higher than the puddling process and 40 times higher than the steelmaking process. The gap between these processes is smaller for the fine particles. When comparing the sintering and puddling processes, the PM_{10} and $PM_{2.5}$ emission factors for the sintering process becomes 5 times and 4.5 times larger than the puddling process, respectively. For the sintering process, the emitted PM_{10} accounts for 37.8% of the TSP, and $PM_{2.5}$ accounts for 27.14% of the TSP. For the puddling process, PM_{10} accounts for 52.3% of the TSP, and $PM_{2.5}$ accounts for 38.1%. For the steelmaking process, PM_{10} accounts for 38% of the TSP, and $PM_{2.5}$ accounts for 24%. Although the PM emission factor for the puddling process is not the highest among all of these processes, the proportion of the fine particles was the greatest.

3.2 Particulate matter profiles of different manufacturing processes

3.2.1 The sintering process

The sintering process was sampled and analysed for all six plants, and the PM chemical profiles are shown in Figure 2.

The PM has been sieved into three levels through the virtual impactor, including $PM_{2.5}$, PM_{10} and $PM_{>10}$. According to the elemental abundances in Figure 2, the identity of the elements of $PM_{2.5}$, PM_{10} and $PM_{>10}$ were consistent within the same plant, but the absolute values for the profiles were varied. For example, Cl increased with PM size for plant D, while it decreased for plant E. In general, SO_4^{2-} , NH_4^+ and OC tend to distribute in smaller particles, making fine particles much more harmful to human health and the climate (Li et al. 2014, Pablo-Romero et al. 2015).

The common elements found in emissions from these plants include Ca, Cl, K,

240 SO_4^{2-} , NH_4^+ and OC, while the relative abundance of these elements at each plant are
241 quite different. For plant A, the content of Ca is close to 50% in $\text{PM}_{2.5}$, and SO_4^{2-}
242 accounts for 10% of the total weight, showing the typical feature of calcium
243 desulphurization. Cl and K are mainly emitted from the raw sintering materials (Zhan
244 et al. 2013), so the Cl and K content of plants B-F are significant, which is in contrast
245 to plant A which has quite low Cl and K contents. These lower levels could be
246 indicative of pollutant control facilities, where the circulating fluidized bed
247 desulfurization coupled with a bag filter shows better performance for Cl adsorption.
248 For the anions, all six plants show high SO_4^{2-} content, closely related to the high SO_2
249 emissions of the sintering process. The NH_4^+ content of plant C and plant D are
250 relatively high, especially plant C which has more NH_3 added by ammonia
251 desulfurization. It can be inferred that PM profiles of the sintering process are greatly
252 impacted by pollutant control facilities. The desulfurizer and the dedusting processes
253 show an instant effect on the chemical compositions. Some harmful heavy metal
254 elements were also detected, such as Pb and Sb. More effective and multi-functional
255 pollutant control technologies should be developed in order to reduce these harmful
256 components.

257 3.2.2 The pelletizing process

258 Limited by the extensively used raw manufacturing process, the number and
259 scale of pellet firing machines in China is far less than the number of sintering
260 machines (Wang et al. 2016), so the pelletizing process was only investigated at one
261 site, plant B. The chemical profiles of $\text{PM}_{2.5}$, PM_{10} and $\text{PM}_{>10}$ of pelletizing process

are shown in Figure 3.

The identity of element emitted from the pelletizing process include Al, Si, S, Fe, SO_4^{2-} and NH_4^+ . Fe is the most abundant element of these components, and its content (38-65%) increased with particle size. SO_4^{2-} is the second highest element from the pelletizing process because of the high SO_2 concentrations emitted; SO_4^{2-} content decreased (36-14%) in larger particles, showing similar changes as the sintering process. The pelletizing process shows low levels of OC content. This profile has not been compared because of the lack of other sampling locations. The pollutant emission standards for the pelletizing process are the same as the sintering process, so the chemical profiles of the pelletizing process will also be affected by pollutant control facilities.

3.2.3 The puddling process

Five puddling processes were sampled in plants B-F, and the PM profiles for the puddling process are shown in Figure 4.

The identity of elements in the puddling process is very simple, with the majority being Fe. All five plants show the same profiles; however, the Fe content varied from 59% to 91%. Other components, such as Ca, Zn, SO_4^{2-} , OC and EC, were dispersed in these five profiles. The distinguishment between $\text{PM}_{2.5}$, PM_{10} and $\text{PM}_{>10}$ is slight, showing good consistency of these profiles.

3.2.4 The steelmaking process

Five steelmaking processes were sampled in plants A-D and plant F, and the PM profiles for the steelmaking process are shown in Figure 5.

The identity of elements from the steelmaking process are close to those found in the puddling process, with Fe content varying from 47% to 78%. Other components, such as Si, Ca, Zn, SO_4^{2-} , exist concomitantly. Ca shows higher content (24-34%) in plant D, which might be related to the raw materials. The differences between $\text{PM}_{2.5}$, PM_{10} and $\text{PM}_{>10}$ are mainly the Fe concentration. Fe content decreased in larger particles for plant B and plant D, while it increased in plant C. The other two plants showed irregular changes in Fe.

3.3 Comparison of $\text{PM}_{2.5}$ and PM_{10} for the different processes

In order to obtain average profiles for the individual processes, a weighted average algorithm based on the amount PM emissions was proposed, and the formula is as follows:

$$\alpha_{i,j,n} = \frac{C_{i,j,n} Q_{j,n} \times \frac{273.15}{(273.15 + T_{j,n})}}{\sum_{n=1}^n C_{i,j,n} Q_{j,n} \times \frac{273.15}{(273.15 + T_{j,n})}} \quad (2)$$

where α is the coefficient of the weighted average; i represents the type of pollutant; Q is the flue gas volume flow, in m^3/h ; T is the flue gas temperature in $^{\circ}\text{C}$; j represents a different production process; and n represents the number of the plant.

For example, the weighted average coefficient of $\text{PM}_{2.5}$ in the sintering process in plant A is marked as $\alpha_{\text{PM}_{2.5}, \text{Sintering}, \text{A}} = 0.0093$.

For the same process, the average profile can be calculated according to a single plant PM profile and the weighted average coefficients as below.

$$F_{i,j,k} = \frac{\sum_{n=1}^n \alpha_{i,j,n} \times F_{i,j,n,k}}{n} \quad (3)$$

where F is the calculated profile value; i represents the type of pollutant; j represents a different production process; n represents the number of the plant; and k represents the chemical species or element.

The average profile of Si in $PM_{2.5}$ emitted in the sintering process is marked and calculated as $F_{PM_{2.5}, Sintering, Si} = 0.1464 \pm 0.0115$. The profiles are displayed in Table 3.

According to the data in Table 3, the chemical species can be divided into crustal matter (Si, Ti, Sl, Mn, Mg, Ca, Fe, K, Na), trace species (Cl, P, Sc, S, V, Cr, Co, Ni, Cu, Zn, As, Se, Br, Sr, Cd, Ba, Pd, Sn, Sb), nitrate, sulfate, ammonium, organic matter, elemental carbon and others, one point should be mentioned is that the S in trace species is rest S of the total S subtract S in sulphate to avoid the overlap calculation. These eight categories of $PM_{2.5}$ and PM_{10} profiles are graphically shown in Figure 6.

Crustal matter, trace species and sulfate are the main components of $PM_{2.5}$ and PM_{10} in iron and steel plants. Sulfate and OC tend to distribute into smaller particles ($PM_{2.5}$). Larger particles (PM_{10}) are mainly composites of crustal matter and trace species. For the sintering process, crustal matter and trace species account for 35% and 32% of the $PM_{2.5}$ respectively; sulfate accounts for 13%, nitrate accounts for 8.9% and OC accounts for 6%. The distribution of components in the sintering process is more complex than the other processes. The high sulfate content of the pelletizing process indicates an urgent need for desulfurization. Crustal matter became the main composition in the puddling and steelmaking processes.

Aiming to identify the distinguishing features and similarities in the PM profiles,

the coefficient of divergence (CD), a self-normalizing parameter used to measure the spread of the data points for two datasets (Kong et al. 2011), was calculated as follows:

$$CD_{jk} = \sqrt{\frac{1}{P} \sum_i^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (4)$$

where j and k indicate the two different PM profiles; P is the number of components; and x_{ij} shows the relative concentration of chemical species i in profile j . If the CD value close to 0, the PM profiles are almost the same. If CD approaches zero, source i and k are similar. If the CD value approaches one, the two profiles are significantly different (Wongphatarakul et al. 1998, Han et al. 2010). A CD value of 0.3 was adopted as a demarcation, where $CD < 0.3$ means the two profiles are similar, and $CD > 0.3$ means the two profiles are different.

CD parameters were initially used to compare the divergence between $PM_{2.5}$ and PM_{10} for same process. The results are shown in Figure 7.

$PM_{2.5}$ and PM_{10} profiles for the same process are similar to each other, with CD values ranging from 0.1697 to 0.2578 (Figure 7), so $PM_{2.5}$ was chosen for the comparison of different processes. The results are shown in Figure 8.

From Figure 8, $PM_{2.5}$ profiles of the four process were different from each other, with CD values ranging from 0.4802 to 0.7500. In the sintering process, the CD values, compared to other processes, are all over 0.6, showing the same conclusions as above.

Furthermore, the differences between the $PM_{2.5}$ profiles of these processes will directly cause uncertainty in the entire iron and steel industry profile. These factors

make it difficult to infer the entire iron and steel industry profiles with insufficient data, showing this topic still needs work to continuously update PM profiles in China.

3.4 PAH analysis of particulate matter

PAHs are formed by incomplete combustion and pyrolysis of organic materials (Ravindra et al. 2008). Sixteen PAHs listed by the US EPA were measured in this study: 12 samples from sintering, pelletizing, puddling and steelmaking processes have been analysed, and the results are shown in Figure 9.

One point should be mentioned regarding Figure 9; the ranges of the Y-axes are quite different among the four processes. The total PAH concentration in PM_{2.5} resulting from the sintering process reaches $73.28 \pm 0.73 \mu\text{g}/\text{m}^3$, while the value for the pelletizing process is only $0.026 \pm 0.0007 \mu\text{g}/\text{m}^3$. PAHs in the puddling and steelmaking processes reach $0.054 \pm 0.0008 \mu\text{g}/\text{m}^3$ and $0.054 \pm 0.0016 \mu\text{g}/\text{m}^3$, respectively. Most of the PAHs in PM are sourced from the sintering process, according the flue gas volume and the sintering production, the emission factor of the total PAHs is calculated at around $0.273 \pm 0.0027 \text{ g/t}$.

The PAHs in PM for the pelletizing, puddling and steelmaking processes are mainly NaP, Acy, Phe, Flu, Pyr, BaA and Chr. These PAH compounds have less than four benzene rings. PAHs from the sintering process mainly include 4 benzene ring PAHs, such as Flu, Pyr, BaA and Chr, and 5 and 6 benzene rings PAHs, such as DBA and BghiP, which might be pyrolysed from the raw materials.

The equivalent toxicity of PAHs was calculated using BaPE (Fang et al. 2004).
$$\text{BaPE} = \text{BaA} \times 0.06 + \text{B[b,k]F} \times 0.07 + \text{BaP} + \text{DBA} \times 0.6 + \text{IND} \times 0.08$$
The BaPE value of

PM_{2.5} for the sintering process in this study is 9.92 µg/m³, 37.6% lower than the value reported by Kong et al. obtained in 2010 (13.65µg/m³) (Kong et al. 2013), which might be affected by the raw materials and the manufacturing processes, however the PAHs components distribution for two work is similar, the majority of PAHs are over four benzene rings, indicating the PAHs in sintering PM are mainly caused by the high temperature cracking of the fossil fuels. So in order to reduce the PAHs emission intensity in the fine particles, pollutants control facilities and the raw material substitution technology should be enforced in China.

4. Conclusions

Source-level sampling method was adopted in this study sampled six iron and steel plants and four main manufacturing processes with over 150 samples were collected and measured in this study. The emission factors of CO₂, CO, SO₂, NO_x, TSP, PM_{2.5} and PM₁₀ in the sintering flue gas are the highest among all the processes, demonstrating the urgency of sintering flue gas purification.

The three PM sizes were divided for chemical profiles, and the identity of elements in PM_{2.5}, PM₁₀ and PM_{>10} are consistent within the same plant. The absolute values for the profiles are varied; SO₄²⁻, NH₄⁺ and OC tend to distribute into the smaller particles. The elements in PM emitted from the sintering process include Ca, Cl, K, SO₄²⁻, NH₄⁺ and OC, and the mass percentage of these elements is greatly impacted by the pollutant control facilities. The elements emitted from the pelletizing process mainly include Al, Si, S, Fe, SO₄²⁻ and NH₄⁺. The lack of desulfurization facility causes SO₄²⁻ to be the second highest for this process. Fe is the main element

in both the puddling and steelmaking processes, with the content varying from 47% to 91%.

The coefficient of divergence was calculated to compare the differences between PM profiles. The divergence between $PM_{2.5}$ and PM_{10} with same process is ambiguous, with CD values ranging from 0.1697 to 0.2578. The $PM_{2.5}$ profiles of the four process were quite different from each other, with CD values ranging from 0.4802 to 0.7500. It is notably difficult to determine the entire iron and steel industry profiles because of insufficient data, so more efforts will be required to update the PM profiles in China. Because of this work is established on the source-level sampling method, the PM condensation part from the flue gas should be added for source appointment.

PAHs from the four process were also investigated, and most of the PAHs in PM are sourced from the sintering process, the majority of PAHs are over four benzene rings, indicating the PAHs in sintering PM are mainly caused by the high temperature cracking of the fossil fuels. The total PAH concentration in $PM_{2.5}$ from the sintering process is $73.28 \pm 1.45 \mu\text{g}/\text{m}^3$, with the BaPE value calculated at $9.92 \mu\text{g}/\text{m}^3$, 37.6% lower than the data obtained in 2010, showing the pollutants control facilities perform synergic remove effect on PAHs emission intensities.

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Figure captions

Figure 1. Schematic of sampling sites for the sintering process

Figure 2. PM chemical profiles for the sintering process

Figure 3. PM chemical profiles for the pelletizing process

Figure 4. PM chemical profiles for the puddling process

Figure 5. PM chemical profiles for the steelmaking process

Figure 6. PM_{2.5} and PM₁₀ profiles for the different processes

Figure 7. The coefficient of divergence between PM_{2.5} and PM₁₀ for the different processes

Figure 8. The coefficient of divergence between the different processes for PM_{2.5}

Figure 9. PAH mass concentrations in PM emitted from various processes

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1. Sampling sites description and flue gas parameters

Plant No.	Process	Collection location	O ₂ (%)	CO ₂ (%)	CO (mg/m ³)	SO ₂ (mg/m ³)	NO _x (mg/m ³)	TSP (mg/m ³)	PM ₁₀ (mg/m ³)	PM _{2.5} (mg/m ³)	T (°C)	Q (m ³ /h)
A	Sintering	Stack after ESP and CFB-FGD	16.27	3.81	293.75	277.14	312	3.9	1.394	0.946	68	64.92×10 ⁴
	Steelmaking	Stack after BF	20.88	0	13.75	0	0	0.5	0.273	0.227	56	47.98×10 ⁴
B	Sintering	Stack after ESP and L-WFGD	15.42	4.52	6987.5	94.29	144.64	121.41	73.89	58.7	59	85.15×10 ⁴
	Pelletizing	Stack after ESP	17.19	3.34	10	520	79.02	10.01	1.32	0.57	125	59.19×10 ⁴
	Puddling	Stack after BF	20.92	0	51.25	14.29	0	8.25	0.69	0.38	56	42.39×10 ⁴
	Steelmaking	Stack after BF	20.78	0	98.75	0	0	1.78	0.36	0.24	54	47.18×10 ⁴
C	Sintering	Stack after ESP and A-WFGD	15.88	6.12	6983	136	131	37.56	11.32	9.37	59	65.39×10 ⁴
	Puddling	Stack after BF	20.93	0	0	0	0	0.89	0.28	0.14	45	17.70×10 ⁴
	Steelmaking	Stack after BF	20.68	0.04	0	0	0	1.18	0.82	0.77	56	22.42×10 ⁴
D	Sintering	Stack after ESP and L-WFGD	16.95	4.05	3941	187	201	46.27	6.62	3.61	54	135.86×10 ⁴
	Puddling	Stack after BF	20.70	0.44	29	0	0	2.32	0.9	0.47	40	13.28×10 ⁴
	Steelmaking	Stack after BF	20.41	0.43	16	0	0	2.99	1.55	0.84	53	31.02×10 ⁴
E	Sintering	Stack after ESP and SDA-FGD	16.82	3.36	5565	225	174	20.17	1.96	0.83	82	152.93×10 ⁴
	Puddling	Stack after BF	20.63	0.09	1220	41	0	16.72	11.78	7.94	72	75.01×10 ⁴

F	Sintering	Stack after ESP and L-WFGD	16.20	5.3	6483	149	127	33.31	18.68	8.85	52	62.07×10 ⁴
	Puddling	Stack after BF	21.00	0	0	0	0	5.06	2.32	1.53	43	57.91×10 ⁴
	Steelmaking	Stack after BF	20.91	0	24	0	0	1.83	0.68	0.39	38	73.60×10 ⁴

ESP: electrostatic precipitator; CFB-FGD: circulating fluidized bed flue gas desulfurization;

BF: bag filter; L-WFGD: lime-gypsum wet flue gas desulfurization; A-WFGD: ammonia wet flue gas desulfurization; SDA-FGD: spraying drying adsorption flue gas desulfurization;

T: flue gas temperature; Q: flue gas volume flow at operating condition

Table 2. Pollutant emission factors of sintering, puddling and steelmaking processes

Process	P(t/h)	K _{CO2} (kg/t)	K _{CO} (kg/t)	k _{SO2} (kg/t)	k _{NOx} (kg/t)	k _{TSP} (kg/t)	k _{PM10} (kg/t)	k _{PM2.5} (kg/t)
Sintering	229	280.6±65.5	16.30±0.09	0.62±0.004	0.62±0.003	0.14±0.001	0.053±0.0008	0.038±0.0006
	— —	220~304 ^a	22 ^b	3.2 ^b	0.6 ^b	1.0 ^b	0.6 ^b	0.5 ^b
	— —	— —	— —	2.4~2.8 ^c	0.52~0.61 ^c	0.40~1.59 ^c	— —	0.211~0.54 ^c
Puddling	146	— —	0.99±0.02	0.038±0.02	— —	0.021±0.0003	0.011±0.0002	0.008±0.0001
	— —	— —	23.7 ^b	0.2 ^b	0.2 ^b	2.0 ^b	1.7 ^b	1.5 ^b
	— —	— —	— —	0.1~0.13 ^c	0.15~0.17 ^c	0.35~1.03 ^c	— —	0.066~0.114 ^c
Steelmaking	133	— —	0.11±0.001	— —	— —	0.005±0.00001	0.0019±0.00001	0.0012±0.00001
	— —	— —	2.96 ^b	0.003 ^b	0.1 ^b	0.41 ^b	0.4 ^b	0.35 ^b
	— —	— —	— —	— —	0.003 ^c	0.16~0.26 ^c	— —	0.14~0.23 ^c

^a Estimated by the material flow analysis (Xu et. al 2016)

^b Estimated by the unite-based bottom-up methodology using data in 2010 (Wang et. al 2016)

^c Estimated by the detailed activity level based on the data between 2008-2012 (Wu et. al 2015)

Table 3. Summary of PM_{2.5} and PM₁₀ chemical profiles (mass percentage, %) for sintering, pelleting, puddling and steelmaking processes

Species	Sintering		Pelletizing		Puddling		Steelmaking	
	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀
Al	0.1120±0.0161	0.1510±0.0220	1.3345±0.1993	1.5818±0.2362	0.3256±0.0486	0.3100±0.0459	0.2559±0.0233	0.2757±0.0407
Si	0.1464±0.0115	0.2291±0.0181	2.5472±0.2032	2.9136±0.2324	0.9678±0.1042	1.0216±0.1162	1.1639±0.0821	1.2320±0.0947
Na	2.0007±0.1206	2.1614±0.1306	0.3199±0.0194	0.3582±0.0217	0.8848±0.0947	0.6373±0.0691	1.0554±0.2586	1.1414±0.0691
Cl	23.2158±1.7195	23.1844±1.7178	0.1158±0.0086	0.1147±0.0085	1.5855±0.1705	1.2833±0.1217	2.2511±0.3698	1.7298±0.1278
Mg	0.1178±0.0116	0.1720±0.0175	0.2542±0.0288	0.2977±0.0337	0.2133±0.0234	0.2145±0.0269	0.6482±0.0557	0.7378±0.0812
P	0.0169±0.0069	0.0176±0.0072	0.1755±0.0723	0.1843±0.076	0.3377±0.2529	0.2554±0.1845	0.1890±0.0521	0.1797±0.0741
S	2.2865±0.2573	2.2273±0.2507	12.4876±1.4055	9.2001±1.0355	2.3046±0.2997	1.8136±0.2507	1.2103±0.4760	1.0915±0.1228
K	13.8629±0.5033	14.0073±0.5085	0.3390±0.0123	0.3653±0.0133	3.2481±0.1247	2.4263±0.0889	2.9684±0.1854	2.2277±0.0810
Ca	16.5145±0.3237	13.9974±0.2688	3.6739±0.0736	4.2776±0.0857	2.5228±0.0593	2.6898±0.0669	6.9561±0.0983	9.2782±0.1843
Sc	0.0093±0.0012	0.0114±0.0015	0.0239±0.0031	0.02510±0.0033	0.0064±0.0001	0.0183±0.0001	0.0200±0.0206	0.0450±0.0058
Ti	0.0263±0.0012	0.0514±0.0023	0.3390±0.0149	0.4865±0.0214	0.1581±0.0148	0.1909±0.0156	0.1617±0.0120	0.1892±0.0104
V	0.0139±0.0027	0.0110±0.0022	0.0370±0.0072	0.0457±0.0089	0.0436±0.0027	0.0475±0.0018	0.0303±0.0006	0.0662±0.0129
Cr	0.0236±0.0012	0.0425±0.0023	0.0442±0.0024	0.0696±0.0037	0.4238±0.0088	0.4248±0.0241	0.1758±0.0414	0.1431±0.0077
Mn	0.0411±0.0053	0.0674±0.0087	0.3975±0.0512	0.5773±0.0744	0.7752±0.0761	0.6477±0.0578	2.5468±0.4590	2.2859±0.2945
Fe	2.6593±0.0430	8.3294±0.1338	38.0058±0.6065	63.1871±1.0084	62.9337±1.0939	64.1883±1.1603	72.6680±0.9233	64.0949±1.0382
Co	0.0028±0.0009	0.0092±0.0028	0.0394±0.0118	0.0580±0.0174	0.0577±0.0061	0.0607±0.0165	0.0596±0.0036	0.0681±0.0204
Ni	0.0147±0.0036	0.0267±0.0066	0.0263±0.0066	0.0309±0.0077	0.1589±0.0239	0.1574±0.0393	0.0490±0.0643	0.0399±0.0100
Cu	0.4301±0.0914	0.3643±0.0774	0.0251±0.0053	0.0309±0.0066	0.0503±0.0310	0.0550±0.0440	0.0407±0.0206	0.0516±0.0110
Zn	0.3647±0.0649	0.3707±0.0660	0.0155±0.0028	0.0206±0.0037	1.8334±1.4811	1.4323±1.0580	1.5646±1.2470	1.3043±0.2319

As	0.0001±0.00000	0.0001±0.0001	0.0740±0.0553	0.0804±0.0600	0.0086±0.0185	0.0060±0.0108	0.0019±0.0026	0.0014±0.0010
Se	0.1926±0.0622	0.1631±0.0527	0.1170±0.0378	0.1121±0.0362	0.0298±0.0006	0.0294±0.0060	0.0250±0.0001	0.0235±0.0076
Br	1.0958±0.2398	1.0185±0.2229	0.0704±0.0154	0.0722±0.0158	0.1265±0.0174	0.1406±0.0176	0.2179±0.0557	0.2462±0.0539
Sr	0.0019±0.0003	0.0017±0.0003	0.0227±0.004	0.0296±0.0052	0.0183±0.0132	0.0270±0.0222	0.0444±0.0204	0.0669±0.0116
Cd	0.0354±0.0025	0.0537±0.0037	0.0585±0.0041	0.0735±0.0051	0.0976±0.0141	0.1403±0.0194	0.2358±0.0270	0.2859±0.0199
Ba	0.0297±0.0015	0.0601±0.0030	0.0859±0.0043	0.0844±0.0042	0.0321±0.0001	0.1193±0.0071	0.2958±0.0008	0.2068±0.0108
Pb	3.3124±0.3622	3.0056±0.3287	0.0561±0.0061	0.0612±0.0067	0.3120±0.0562	0.2561±0.0504	0.4507±0.1647	0.4425±0.0484
Sn	0.0655±0.0100	0.0943±0.0144	0.1289±0.0198	0.1321±0.0202	0.1418±0.0003	0.1995±0.0004	0.3404±0.0012	0.4372±0.0670
Sb	3.6541±0.1106	3.7733±0.1142	0.1349±0.0041	0.1379±0.0042	0.8006±0.0272	0.6580±0.0271	0.7346±0.0518	0.6160±0.0187
NO ₃ ⁻	0.5228±0.0046	0.4915±0.0043	0.2080±0.0018	0.05610±0.0005	0.4864±0.0009	2.5653±0.0021	0.0253±0.0003	0.8394±0.0074
SO ₄ ²⁻	13.0426±0.2240	12.3804±0.2127	36.8721±0.6335	14.2077±0.2441	7.0717±0.0278	6.5849±0.0244	0.8001±0.0112	8.0301±0.1380
NH ₄ ⁺	8.9182±0.0759	7.6223±0.0649	1.9706±0.0168	1.1278±0.0096	2.2678±0.0006	1.7065±0.0004	0.0288±0.0003	0.0497±0.0004
OC	6.0057±0.1802	4.9582±0.1488	0.0000±0.0000	0.0000±0.0000	4.0097±0.0149	4.2022±0.0138	0.2714±0.0214	0.2082±0.0062
EC	0.3169±0.0094	0.2286±0.0068	0.0000±0.0000	0.0000±0.0000	4.1656±0.0015	3.8903±0.0014	0.0000±0.0000	0.0000±0.0000