Characteristics of PM_{2.5} and polycyclic aromatic hydrocarbons emitted from coal combustion processes

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Introduction

Airborne particulate matter (PM), especially PM_{2.5}, has caused serious environmental and health problems. Ambient PM contains a large number of pollutants, such as polycyclic aromatic hydrocarbons (PAHs), heavy metal, acidic oxides and dioxin [1]. PAHs are a group of compounds composed of two or more benzene rings. They are generated by the incomplete combustion or pyrolysis of fossil fuels. PAHs have caused great public concern due to their mutagenicity and carcinogenicity [2, 3]. Coal-fired processes are regarded as one of major stationary sources of PM and PAHs. Many studies have been conducted to evaluate PM and PAHs emissions from coal-fired processes. PM emitted from coal-fired processes consist of filterable particulate matters (FPM) and condensable particulate matters (CPM). U.S. EPA Method 202 defines CPM as material that is in the vapor phase under stack conditions, but condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. Due to some uncertainties in the CPM measurement [4], the difference among various studies needs to be clarified. In this study, we collected the samples from two coal-fired processes in Taiwan. Plant A is a coal-fired power plant while Plant B is food processing plant equipped with a coal-fired boiler. The flue gas samples were collected at the stack in each coal-fired process and inlet of baghouse at Plant A to investigate the removal efficiency of PM and PAHs and also understand the congener distribution.

Materials and methods

The flue gas samples are simultaneously collected at inlet of BH and the stacks in plant A. FPM measurement was conducted according to U.S. EPA Method 201A and CPM measurement was carried out based on U.S. EPA Method 202. The PAHs sampling train is comprised of a sampling probe, a filter holder, an XAD-2 trap, a thermocouple, impingers, an ice bath, an air-tight pump and a dry gas meter. During the sampling, the gas-phase sample was collected using XAD-2 resin while the solid-phase sample was collected using a fiber glass filter at 130°C, with subsequent rinsing of the sampling probe. A total of 2–3h was required to perform each PAH sampling [5]. Figure 1 shows the flow chart of two coal-fired processes and sampling sites. FPM concentration was analyzed by measuring the weight increase of the filter. CPM filter was extracted twice by water and then by hexane in the ultrasonicator [6]. The aqueous (water soluble) and organic (organic solvent soluble) fractions

were dried and weighed in laboratory. Condensable PM2.5 is the summation of the two fractions. PAHs samples were extracted for 16 h by Soxhlet extraction with dichloromethane. An isotope-spiked solution of PAHs was added before sample extraction to quantify the concentration of each PAH congener. The dichloromethane extract was then concentrated to approximately 2 mL by rotary evaporation and was replaced by 8 mL hexane. Then, the sample was passed through a clean-up column that was packed with activated silica gel. The column was eluted to obtain PAHs in the purifying solution and condensed to 5 mL by rotary evaporation. The collected eluent was reconcentrated to 450 μ L with nitrogen for analysis. The samples were analyzed by HRGC/HRMS using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 m).



Figure 1 Flow diagram and sampling site of plant A and B

Results and discussion:

The concentration of filterable particulate matter (FPM_{2.5}) emitted from plant A (0.44-0.46 mg/Nm³) is significantly lower than that from plant B (1.77-2.05 mg/Nm³). In plant A, the removal efficiency of FPM_{2.5} achieved with the APCD (baghouse and seawater flue gas desulfurization) reaches 99.8%. The TPM concentration measured at BH inlet of plant A is 4,923 mg/Nm³ and PM_{2.5} accounts for only 5.38% of TPM. On the other hand, TPM concentration measured in stack decreases significantly to 0.59 mg/Nm³, indicating that the TPM removal efficiency reaches 99.9%, but the ratio of PM_{2.5}/TPM increases significantly to 76%. For plant B, TPM concentration of stack gas is 2.55 mg/Nm³ and PM_{2.5} accounts for 75% of TPM. The FPM_{2.5} concentration in plant B is higher than that of plant A. Moreover, concentration of CPM in plant B (24.6-34.0 mg/Nm³) is also significantly higher than that of plant A (11.3-13.9 mg/Nm³). It's worth noting that the removal efficiency of CPM achieved with BH and SWFGD in plant A is 38.3%, which is significantly lower than that of FPM_{2.5} ($\eta = 99.8\%$) and TPM ($\eta = 99.9\%$), as presented in Table 1. The emission factors of TPM, FPM and CPM of plants A

and B based on coal consumption are presented in Figure 2. The emission factors of TPM, FPM and CPM are 6.89, 5.25 and 142 g/ton-coal for plant A, respectivity. On the other hand, the emission factors of TPM, FPM and CPM are 26.8, 20.1 and 307 g/ton-coal for plant B, respectivity. In terms of overall performance, plant B emitted higher concentration of PM than plant A due to different APCDs equipped and operating conditions.

Sampling site	Temperature at the stack (°C)	FPM concentration	TPM concentration	CPM concentration	FPM/TPM ratio	CPM/TPM ratio
Plant A	105	0.46	0.59	11.3	0.77	19.1
	106	0.44		13.9	0.75	23.5
	105	0.44		11.3	0.74	19.1
Plant B	59.1	1.77	2.55	24.6	0.69	9.65
	58.9	2.05		34	0.80	13.3

Table 1 TPM, FPM and CPM concentrations measured in plant A and B (unit: mg/Nm³)



Figure 2 Emission factors of TPM, FPM and CPM in plant A and B



Figure 3 PAHs concentrations of measured at BH inlet and stack in plant A, respectively.

Although total PAHs concentrations were relatively high in both plants, the distribution of gas phase and solid phase were significantly different. Gas-phase PAHs and solid-phase PAHs concentrations emitted from plant A are 20.3-34.0 µg/Nm³ and 111-137 ng/Nm³, respectively. For plant A, the removal efficiency of PAHs is higher than 96% for solid-phase PAHs, but varies between 64%-95% for gas-phase PAHs. In comparison, plant B emits more gas-phase PAHs (35-50 µg/Nm³) and solid-phase PAHs (156-285 µg/Nm³) if compared with plant A. The low-rings (1-3 rings) PAHs were the major congeners of both plants in total concentration, such as Ace, Phe and Nap. The 4-6 rings PAHs were relatively lower than low-ring PAHs. Due to relatively higher vapor pressure, low molecular weight (LMW) PAH compounds, are easier to be volatilized and desorbed from particulate matter into the gas phase. In this study, lower HMW PAH concentration measured in stack gas compared with LMW PAH could be attributed to the high removal efficiency of PM.



Figure 4 PAHs concentration emitted from plant B

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