

Group Separation of Water-soluble Organic Carbon Fractions in Ash Samples from a Coal Combustion Boiler

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ABSTRACT

The chemical characterization of water-soluble organic carbon in ash emitted from a coal combustion boiler has not been reported yet. A total of 5 ash samples were collected from the outlet of an electrostatic precipitator in a commercial 500 MW coal-fired power plant, with their chemical characteristics investigated. XAD7HP resin was used to quantify the hydrophilic and hydrophobic water-soluble organic carbons (WSOC), which are the fractions of WSOC that penetrate and remain on the resin column, respectively. Calibration results indicate that the hydrophilic fraction includes aliphatic dicarboxylic acids and carbonyls (<4 carbons), amines and saccharides, while the hydrophobic fraction includes aliphatic dicarboxylic acids (>4-5 carbons), phenols, aromatic acids, cyclic acid and humic acid. The average mass of the WSOC in the ash samples was found to depend on the bituminous coal type being burned, and ranged from 163 to 259 $\mu\text{g C/g}$ of ash, which corresponds to 59-96 mg C of WSOC/kg of coal combusted. The WSOC mass accounted for 0.02-0.03 wt% of the used ash sample mass. Based on the flow rate of flue gas produced from the combustion of the blended coals in the 500 MW coal combustion boiler, it was estimated that the WSOC particles were emitted to the atmosphere at flow rates of 4.6-7.2 g C/hr. The results also indicated that the hydrophilic WSOC fraction in the coal burned accounted for 64-82% of the total WSOC, which was 2-4 times greater than the mass of the hydrophobic WSOC fraction.

Key words: Coal combustion, Ash, WSOC, XAD7HP resin

1. INTRODUCTION

A significant fraction of particulate organic matter is water-soluble organic carbon (WSOC), which is

commonly found in particles internally mixed with inorganic species. WSOC may affect the hygroscopic properties of aerosol particles and the ability of particles to serve as cloud condensation nuclei (CCN) (Faccini *et al.*, 1999; Saxena *et al.*, 1995). WSOC, specifically, may increase the solubility of organic-laden particles or depress the surface tension of aqueous solutions (Kiss *et al.*, 2005). Moreover, the absorption of visible and UV light by WSOC constituents of smoke particles, including those dissolved in cloud droplets, contribute to the positive radiative forcing of the climate (Chen and Bond, 2010; Andreae and Gelencsér, 2006; Hoffer *et al.*, 2006).

An organic aerosol is a highly complex mixture, composed of oxygenated carbon functional groups; thus, making the comprehensive chemical characterization of aerosol OC using gas chromatography-mass spectrometry (GC-MS) difficult (Decesari *et al.*, 2000). The isolation of the WSOC fraction has focused on the classification of organic aerosols into broad and comprehensive chemical fractions. These WSOC compounds can be broadly classified into hydrophilic and hydrophobic fractions (Miyazaki *et al.*, 2009; Durate and Duarte, 2005). The hydrophilic WSOC fraction tends to be highly soluble in water, and includes compounds with low molecular weights, such as aliphatic carboxylic acids and carbonyls (<4 carbons), saccharides, and amines; whereas, the hydrophobic WSOC fraction tends to be less hygroscopic and includes aliphatic carboxylic acids and carbonyls (>3-4 carbons), aromatic acids, phenols, organic nitrates and cyclic acids, as well as Suwannee River fulvic acids. To better understand the sources and atmospheric processing of organic aerosol particles, a comprehensive study is required via the isolation of the organic compounds in aqueous solutions according to their chemical functional groups.

Coal is an important energy resource to meet the future demand of electricity because its reserve is more abundant than those of the other fuels. At present, coal-fired power plants generally involve pulverized coal combustion. During coal combustion, the minerals in

coal are transformed into ash particles that are different in size and chemical composition. Some trace elements in the minerals are known to be present in association with organic materials (Richaud *et al.*, 2000). The combustion of organic volatiles being released from the coal can take place close to the surface of the particle, immediately after they are ejected from the porous structure, or at some distance from the surface. Typically the organic volatiles mix with air during their release from the particle. The following features are important in the combustion of organic volatiles; release of volatiles from coal, cracking of hydrocarbons to lower molecular weight hydrocarbons with local production of soot, condensation of gaseous hydrocarbons and agglomeration of soot particles, oxidation of gaseous species to combustion products, etc. (Kurose *et al.*, 2001). It has long been known that submicron sized particles from the combustion of coal are primarily formed by the condensation of vaporized ash, soot and char particles (Senior and Flagan, 1982; Flagan and Friedlander, 1978). The major constituents of the submicron ash particles are the same as those forming the bulk of the ash; however, their relative contributions vary significantly from that of the bulk ash. The composition of coal has been shown to be an important parameter affecting the amount and composition of the submicron ash particles formed.

The main pollutants considered in a coal-fired power plant are solid particles, SO₂, NO_x and CO. In recent years, despite many advances in relation to the particulate organic aerosol composition in the atmosphere, the chemical characterization of the WSOC in the ashes produced from commercial pulverized coal combustion boilers has not been reported yet. To the best of our knowledge, this study is the first to report on the group separation of WSOC fractions in ash samples emitted from a coal-fired power plant. In this paper, the results of the group separation of WSOC fractions in ash samples collected from a commercial 500 MW coal-fired power plant are reported. XAD7HP resin, with TOC (total organic carbon) detection, was used to separate the WSOC into the hydrophilic and hydrophobic fractions.

2. MATERIALS AND METHODS

2.1 Collection of Ash Samples from a Commercial 500-MW Pulverized Coal-fired Boiler

A total of 5 ash samples were collected from the outlet of an electrostatic precipitator at one of "H" coal-fired power plants (CFPPs). An ash sample was

Table 1. Properties of the coals used in a 500-MW coal-fired boiler (as air-dry basis).

Coal type	A	B	C	D	E
Proximate analysis					
Moisture (%)	4.8	13.5	10.9	14.5	8.8
Ash (%)	31.0	37.7	39.6	38.6	40.0
Volatile matter (%)	15.7	7.0	1.1	4.9	8.6
Fixed carbon (%)	48.5	40.8	38.5	42.0	42.7
Ultimate analysis					
Carbon (%)	68.7	68.6	66.3	69.5	68.5
Hydrogen (%)	4.4	4.8	5.0	4.7	4.9
Nitrogen (%)	1.5	1.4	1.2	1.6	1.6

taken once a day. In Korea, oil- and coal-fired power plants have operated for base load power generation. The "H" power plants consist of eight pulverized coal-fired boilers, with generating load capacities of 4,000 MW (500 × 8 units). 150 m high stacks at the "H" power plants are equipped with electrostatic precipitators and a wet flue gas desulfurization (FGD) system for the control of particulate and SO₂ emissions. In Korea, coal blending has been used to provide a consistent feedstock of fuel for the power generation industry. Blending may also be used to reduce the costs and compensate for the undesirable characteristics of a coal, such as the sulfur content. "H" coal-fired boilers use many different types of bituminous coals to generate super-saturated steam and electricity. Coals of five types were used in the boiler. Their proximate and ultimate properties are shown in Table 1. On an air-dry basis, the fixed carbon and volatile matter contents were found to range from 38.5 to 48.5% and 4.9 to 15.7%, respectively, depending on the coal type. The ash contents were ranged from 31.0 to 40.0% depending on the type of coal. Five pairs of blends, with dissimilar properties, were formulated from the component coals (based on weight %): A80B20 (80%A, 20%B), A50B50 (50%A, 50%B), A30C70 (30%A, 70%C), A30D70 (30%A, 70%D), and A40E60 (40%A, 60%E).

2.2 Chemical Characterization of Ash Samples

2.2.1 Chemical Analyses of Ionic Species and Bulk WSOC

The collected ash samples (~50 mg each) were extracted with 40 mL of ultrapure distilled de-ionized water ("DDW", 18.2 MΩ) produced from ultrapure water purification system (Barnstead Nanopure, #D11901, Thermo Scientific, USA) via ultrasonication for 60 min. The water extracts were filtered using a syringe membrane filter (Millipore 0.45 μm) to remove the insoluble particles and then analyzed for the determina-

tion of eight ionic species (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}), as well as their bulk WSOC contents, using ion chromatography (IC, Metrohm 861) and an total organic carbon analyzer (TOC, Sievers 5310C, USA), respectively. In the TOC analyzer, the organic compounds dissolved in ultrapure water were oxidized to form carbon dioxide using an ultraviolet (UV) lamp and ammonium persulfate as the chemical oxidizing agent. The CO_2 formed was then measured using a membrane-based conductivity detection technique. The remaining extracts were used for the group separation of the bulk WSOC materials, as discussed below. The TOC concentrations for the ultrapure distilled water used for extracting ash samples and cleaning the resin column were in the range of 10-15 ppb. This background level was used to correct bulk WSOC concentrations in fly-ash samples.

2.2.2 Group Separation of Bulk WSOC Fractions Using XAD Resin Method

In order to separate the total WSOC into its hydrophilic and hydrophobic fractions, XAD7HP resin (Rohm & Haas France S.A.S) was used. Some previous studies have used XAD-8, DAX-8, or OASIS HLB resin to isolate WSOC hydrophobic fractions from ambient air samples (Miyazaki *et al.*, 2009; Sullivan and Weber, 2006; Varga *et al.*, 2001). Because XAD-8 resin is no longer commercially available, a substitute resin, XAD7HP, was used in this study. The organic compounds retained on the resin were strongly related to the hydrophobic components of the WSOC, while the organic compounds that passed through the XAD7HP column were the more hydrophilic fractions. XAD7HP resin, a polymeric adsorbent, is available as white insoluble beads. The XAD7HP adsorbent was cleaned prior to use until the organic compounds and salts had been removed from the adsorbent. In this work, the resin was primarily pre-treated with methanol and acetone for 48-hr each using a Soxhlet extraction apparatus. This primary washing cycle was repeated three times. After the Soxhlet treatments the resin was washed with DDW for 2.1 hr to eliminate the residual solvent. For the group separation of the WSOC, a 6 mm ID \times 10 cm long aqueous chromatography column (Spectrum Laboratories, Inc., Houston, TX, USA), hand-packed with the resin, was used. Before the washed resin was loaded into the column, it was cleaned again with DDW for 2.1 hr. Before the sample extracts were continuously pumped onto the XAD7HP resin, the washing cycle of the resin column consisted of alternating 0.1 M NaOH and 0.1 M HCl for 20 min each, all at flow rates of 2.0 mL/min by a multi-channel peristaltic pump (Ismatec IPC-N-16). An intermediate washing step with DDW was carried

out between alkali and acid treatments. This NaOH-HCl cycle was repeated three times. After all the washing procedures had been completed, the resin column was tested three times with DDW. The DDW passing through the column was analyzed using the TOC analyzer to check the quality of the washing. The TOC levels before (“total WSOC”) and after (“hydrophilic WSOC”) passing through the resin column were observed to be 10-15 ppb and 7-10 ppb, respectively, which may be negligible. This result implies that the washing quality of the resin used was fairly good. The average blank values were used as background subtraction for each ash sample. Prior to loading, the aqueous sample solution was adjusted to pH 2 with HCl, and then introduced to the XAD7HP resin column at a rate 2.0 mL/min, using a peristaltic pump. The sample flow rate through the column was maintained at 1.3 mL/min for 20 min. In this study, the organic compounds that passed through the XAD7HP column were measured using the TOC analyzer, and referred to as the hydrophilic fraction. The difference between the total and hydrophilic WSOC was defined as the hydrophobic WSOC fraction. The analytical uncertainties in the total WSOC and hydrophilic WSOC measurements made with the ultrapure water were estimated to be $\pm 7\%$ and 10% , respectively.

2.3 Laboratory Calibration for the XAD7HP Resin Using Organic Compounds Standards

To characterize the performance of the XAD7HP resin, the penetration efficiency was tested using a variety of water-soluble organic compounds relevant to atmospheric aerosols. These experiments were carried out for a couple of concentrations (100-400 μg C/L of water) of organic standard solutions for the tested compounds. The organic compounds selected in this test, as well as their penetration results are summarized in Table 2. In this study, based on the triplicate analyses of the same organic standard samples, the analytical error was estimated at $< \pm 8\%$. Some studies have shown that WSOC is composed of compounds, such as aliphatic acids, carbonyls, aromatic acids, saccharides, polyols, phenols, organic nitrates, humic acids, and amines (Sullivan and Weber, 2006; Durate and Duarte, 2005). These compounds can be broadly classified into hydrophilic and hydrophobic fractions. Hydrophilic and hydrophobic in the last column of Table 2 indicate the WSOC compounds that passed through or were retained on the column at pH 2, respectively. The resulting penetration efficiencies of the resin remained relatively unchanged with the concentration of the organic species. The experimental results indicated that aliphatic dicarboxylic acids and car-

Table 2. Results of the XAD7HP penetration tests for a variety of water-soluble organic compounds listed by functional groups.

Functional group	Standards	Concentration ($\mu\text{g C/L}$)	Penetration (%)	Property
Dicarboxylic acid	Oxalic acid(2)*	83, 105, 210, 412	87, 92, 100, 103	Hydrophilic
	Malonic acid(3)	103, 226	79, 73	Hydrophilic
	Succinic acid(4)	184, 372	92, 95	Hydrophilic
	Maleic acid(4)	163, 352	98, 99	Hydrophilic
	Fumaric acid(4)	165, 362	0, 0	Hydrophobic
	Glutaric acid(5)	156, 214	42, 8	Hydrophobic
	Adipic acid(6)	114, 189	0, 1	Hydrophobic
	Azelaic acid(9)	229, 415	17, 0	Hydrophobic
Carbonyl	Glyoxal(2)	97, 200	105, 96	Hydrophilic
	Methyl glyoxal(3)	117, 252	114, 96	Hydrophilic
Amines	Ethanolamine	86, 202	70, 101	Hydrophilic
Saccharide	Levoglucozan	208, 418	89, 97	Hydrophilic
	Sucrose	207, 395	91, 94	Hydrophilic
Phenols	Catechol	196, 402	0, 0	Hydrophobic
	Syringaldehyde	204, 400	0, 0	Hydrophobic
Aromatic acids	Phthalic acid	191, 390	0, 0	Hydrophobic
Cyclic acid	cis-Pinonic acid	200, 399	17, 3	Hydrophobic
Humic-like	Humic acid	181, 396	0, 0	Hydrophobic

Note)*Listed in parentheses is the number of carbon atoms per molecule for the series mono- and di-carboxylic acids and carbonyls.

Table 3. Chemical characterization of ash samples collected from a commercial 500 MW coal combustion boiler.

Sample description	Ash1	Ash2	Ash3	Ash4	Ash5	GRAND
Coal blending (wt %)	A80 : B20	A50 : B50	A30 : C70	A30 : D70	A40 : E60	Average
Ionic species						
NO ₃ ⁻ (wt %)	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
SO ₄ ²⁻ (wt %)	0.29±0.00	0.39±0.00	0.34±0.00	0.29±0.00	0.36±0.00	0.33±0.04
Na ⁺ (wt %)	0.01±0.00	0.02±0.00	0.02±0.00	0.02±0.00	0.01±0.00	0.01±0.01
NH ₄ ⁺ (wt %)	0.00±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.02±0.00	0.01±0.00
K ⁺ (wt %)	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
Ca ²⁺ (wt %)	0.19±0.03	0.30±0.02	0.36±0.01	0.46±0.02	0.53±0.01	0.37±0.13
Mg ²⁺ (wt %)	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Water-soluble OC fractions						
Total WSOC (mg C/kg of coal)	63±6	88±7	96±6	59±7	69±13	75±16
Hydrophilic WSOC (mg C/kg of coal)	51±8	70±12	78±31	38±9	44±15	49±18
Hydrophobic WSOC (mg C/kg of coal)	12±2	18±19	18±26	21±15	25±2	26±13

Note) A80 : B20 in the ash1 sample indicates a coal mixture of "A" coal of 80% by weight and "B" coal of 20% by weight.

bonyls (<4 carbons), amines and saccharides were hydrophilic WSOC. Noted: levoglucozan, known as a marker of biomass burning emissions (Simoneit *et al.*, 2004), was included as hydrophilic WSOC. The hydrophobic WSOC included aliphatic dicarboxylic acids (>4-5 carbons), phenols, aromatic acids and cyclic acid, as well as Suwannee River fulvic acid. Although only a limited number of the standards were tested, our results were very similar to those reported in other studies (Miyazaki *et al.*, 2009; Durate and Duarte, 2005).

3. RESULTS AND DISCUSSION

3.1 Group Separation of WSOC in Extracts of Ash Samples

Table 3 shows the chemical analyses of the 5 ash samples collected from the outlet of an electrostatic precipitator of a 500 MW pulverized coal combustion boiler. The average concentrations of WSOC in Ash1 ("A80B20"), Ash2 ("A50B50"), Ash3 ("A30C70"), Ash4 ("A30D70") and Ash5 ("A40E60") samples were 196, 256, 259, 163 and 190 $\mu\text{g C/g}$ of ash, respectively,

accounting for 0.02, 0.03, 0.03, 0.02, and 0.02% (by weight) of the weight of the ash samples used, respectively. The respective WSOC concentrations correspond to 63, 88, 96, 59, and 69 mg C/kg of coal combusted, with an average of 75 ± 16 mg C/kg of coal combusted. The WSOC contents in the ash samples were found to be noticeably low, but huge amounts of the ash were emitted to the atmosphere through the stacks, with an emission of 20 mg/m³ per 500 MW boiler. Based on the flue gas flow rate of 1,397,520 m³/hr, it was estimated that the WSOC particles were emitted to the atmosphere at a flow rate of 4.6-7.2 g C/hr. The concentrations of the hydrophilic WSOC fraction ranged from 38 to 78 mg C/kg of coal combusted, accounting for 64 to 82% of the total WSOC, implying that significant amounts of hydrophilic compounds were emitted to the atmosphere through the stacks. These results could be utilized to evaluate the impact of coal combustion power plants on WSOC levels at a region where coal fired power plants are not far away from a sampling site.

4. CONCLUSIONS

The WSOC particles in ambient air are known to be emitted directly from combustion, industrial, and natural sources (primary) and/or are formed through atmospheric processing. However, to the best of our knowledge, this study is the first to report the results of bulk and chemically fractionated (hydrophilic and hydrophobic) WSOC in the dusts emitted from a utility-scale coal-fired power plant using a macro-porous nonionic (XAD7HP) resin column. A total of five ash samples were collected from the downstream of electrostatic precipitator in a 500 MW coal-fired power plant and used for quantification of the bulk, hydrophilic and hydrophobic WSOC. The experimental results showed that the total WSOC depended on the coal type used, ranging from 59 to 96 mg C/kg of coal combusted. Group separation of the aqueous extracts of the ash samples indicated that the mass of the hydrophilic WSOC fraction was higher than that of the hydrophobic WSOC by a factor of 2-4. This study could provide an improved understanding of the emission sources of organic aerosols to the real atmosphere.

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