Atmos. Chem. Phys. Discuss., 13, 3345–3377, 2013
www.atmos-chem-phys-discuss.net/13/3345/2013/
doi:10.5194/acpd-13-3345-2013

Atmospheric
Chemistry
and Physics
Discussions
Open Access

Characterization of organic aerosol produced during pulverized coal combustion in a drop tube furnace

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Received: 19 October 2012 – Accepted: 23 January 2013 – Published: 6 February 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Controlled bench scale pulverized coal combustion studies were performed that demonstrate that inorganic particles play a critical role as carrier of organic species. Two commonly-used aerosol mass spectrometry techniques have been applied to characterize fine particle formation during coal combustion. It was found that the organic species in coal combustion aerosols have similar mass spectra as those from biomass combustion. Ambient measurements in Shanghai, China confirm the presence of these species in approximately 36 ∼ 42 % of the sampled particles. With the absence of major biomass sources in the Shanghai area, it is suggested that coal combustion may be the main source of these particles. This work indicates there is a significant potential for incorrect apportionment of coal combustion particles to biomass burning sources using widely adopted mass spectrometry techniques.

1 Introduction

Pulverized coal combustion is widely used worldwide for the production of electricity; accounting for 45 % of electricity generation in the United States, to greater than 70 % in India and China (Biswas et al., 2011). Coal combustion is a major primary source of atmospheric aerosol (Seinfeld and Pandis, 2006), which affects climate and human health (Poschl, 2005). While the characterization and fate of the mineral matter component of coal during combustion has been well studied and understood (Biswas and Wu, 1998; Linak and Wendt, 1994; Zhuang and Biswas, 2001), the characterization and fate of corresponding organic matter content has not yet been examined in detail. Although a few field studies suggested that primary particulate organic carbon emission from some power plants is very low (Zaveri et al., 2010; Peltier et al., 2007), power plants with lower combustion efficiency may still produce a significant amount of carbonaceous aerosol, including both black carbon and organic aerosol (OA), particularly in some developing countries where particle control technology is not extensively used

Some studies (Huggins et al., 2004; Shoji et al., 2002) report that particulate matter from coal combustion contained significant fraction (up to 13 ∼ 16 % by mass) of carbonaceous matter. Therefore, in recent years, there has been renewed interest in the organic matter content of coal fly ash, due to potential impacts on both climate change and human health (Zhuang and Biswas, 2001; Cho et al., 2009; Jacobson et al., 2000).

Particulate matter formation is closely associated with the burning of coal particles, which occur in 3 steps (as illustrated in Fig. S1) (Warnatz et al., 2006): (a) pyrolysis of coal: molecular structure of coal can be represented by clusters of many fused aromatic rings connected with other clusters via aliphatic bridges or loops. The aromatic bonds are very stable compared to the aliphatic bridges and loops. These bridges break up first during the heating of the coal particles. Some aromatic cluster fragments with lower molecular weights, referred to as "tar", are released into the gas phase due to their higher volatility. Meanwhile, larger molecular-weight fragments remain in parent coal particles due to their lower volatility. The remaining particle is called "char"; (b) burning of tar: tar molecules that have been released to the gas phase are rapidly oxidized; (c) burning of char: char is basically a mixture of carbon clusters and inorganic ash. The carbon on the char surface first reacts with CO_2 and forms CO. Then, the CO is oxidized in the gas phase.

According to our knowledge, only a few studies have characterized particulate organic emissions from pulverized coal combustion (Zhang et al., 2008; Linak et al., 2007). Zhang et al. (2008) measured emission factors of organic carbon and elemental carbon for both industrial boilers and residential stoves. They found 48–68 % of particulate organic matter is organic acids. The main components also include polycyclic aromatic hydrocarbons (PAHs) and alkanes.

Organic matter may relate with soot particle formation from combustion. There are some studies which have investigated the formation mechanisms of soot particles from coal combustion. Brown and Fletcher (1998) proposed tar is the precursor to soot formation during coal combustion. Tar molecules have relative larger molecular weight, which allow them to form soot by directly losing H, O and other atoms, without forming polycyclic aromatic hydrocarbons (PAHs). Rigby et al. (2000) found that soot yields decreased if flame temperature is increased. And soot yields increased if the residence time of coal particles in the flame is increased, indicating that light-hydrocarbon may be incorporated in the soot in the flame. Linak et al. (2007) reported the carbon content in ultrafine particles (diameter < 500 nm) produced from coal combustion. They also found the carbon content was correlated with toxicity of the particles. Drop-tube furnace reactors have been widely used to investigate pulverized coal combustion in laboratory (Card and Jones, 1995; Cloke et al., 2002; Visona and Stanmore, 1999, Suriyawong et al., 2006; 2008), due to its well-controlled temperature profile, gas composition and residence time.

In this study, pulverized coal particles were combusted in a drop-tube furnace that was coupled with various aerosol instrumentation. Various mass spectrometry techniques such as thermal vaporization aerosol mass spectrometry and laser ablation single particle mass spectrometry were used to characterize and unravel the mechanistic details of the pathway of the organic species during aerosol formation in coal combustors. These results were then used to apportion the ambient aerosol in Shanghai to coal combustion sources.

2 Experimental

2.1 Experimental setup and test plan of bench-scale pulverized coal combustion

As shown in Fig. 1, the experimental setup consists of a drop-tube furnace (Lindberg/Blue M, Model HTF55342C, ThermoElectron Corp., USA) with an alumina tube (5.72 cm inner diameter and 121.92 cm long), a scanning mobility particle sizer (SMPS, TSI Inc., Shoreview, MN, USA), a high-resolution time-of-flight aerosol mass spectrometer (HR-Tof-AMS, Aerodyne Research Inc, MA, USA) and other supporting instruments Pulverized Powder River Basin (PRB) sub-bituminous coal (coal particle diameter ≤ 50 µm) was fed using a coal feeder (design of the feeder has been published elsewhere, Quann et al., 1982) into the drop-tube furnace at feed rates ranging from 1 to 3.5 $\mathrm{g\,h^{-1}}$. 1 $\mathrm{L\,min^{-1}}$ (LPM) carrier gas (air or air/N_2 mixture) was used in the coal feeder and carried coal particles into the furnace. Another 2 LPM carrier gas was introduced into the furnace directly. Total 3 LPM air or additional-N_2/air mixture was fed at the inlet to the furnace and passed through the alumina tube with coal particles. In this study, the wall temperature of the alumina tube was fixed at 1373 K. Coal particles can be combusted completely when they travel through the alumina tube. At the exit of the combustor, 5 LPM particle-free air was added as primary dilution. The diluted exhaust gas passed through a six-stage cascade impactor (Mark III, Pollution Control System Corp., Seattle, WA) to remove particles with diameter larger than 500 nm. A slip stream with low flow rate was mixed with high flow rate (details shown in Table 1) particle-free air to achieve a secondary dilution after the impactor. A SMPS was used to obtain the particle size distribution in the range 9 ∼ 425 nm. Particulate organic matter was characterized by a thermal vaporization aerosol mass spectrometer (AMS, Aerodyne Research Inc.). Fine particles were also collected by quartz filters for further analysis. All experimental conditions are summarized in Table 1. Coal feed rates and gas compositions were changed in order to investigate formation mechanisms of OA during coal combustion.

2.2 High-resolution time-of-flight aerosol mass spectrometer (HR-Tof-AMS)

The Aerodyne quadrupole Aerosol Mass Spectrometer (Q-AMS) has described in detail by Canagaratna et al. (2007); Allan et al. (2003); and Jimenez et al. (2003). HR-Tof-AMS is a newer version of AMS and has better mass-to-charge ratio (*m/z*) resolution and faster response than the Q-AMS. The HR-Tof-AMS has been described in detail by DeCarlo et al. (2006). Briefly, aerosol particles are introduced into the AMS via the aerodynamic lens, which focuses the particles into a narrow beam. Particle size is resolved based on particle velocity across a time of flight chamber at the exit of the aerodynamic lens. Next, particles are impacted on a vaporizer where the non-refractory fraction is vaporized and immediately ionized using electron impact ionization. Finally, these ions are analyzed by a time-of-flight mass spectrometer. The vaporizer temperature was set to 600 °C. Coal combustion produces CO_2, which will also contribute to some organic peaks like *m/z* 28 and 44. A set of control experiments (filtered, particle-free exhaust gas measured by AMS was used as the baseline) were conducted to determine and subtract the contribution of organic signal from CO_2. By using high-resolution mass spectra, the exact molecular formula of each organic peak (e.g. $C_xH_yO_z$) was obtained, and overall elemental ratios for the entire mass spectrum was calculated. The method of calculation has been described by Aiken et al. (2007).

2.3 Aerosol time-of-flight mass spectrometer (ATOFMS)

The design and operation of ATOFMS (Model 3800, TSI Inc. Minnesota, USA) have been described by Gard et al., (1997). Aerosols (with the diameter in the range from 0.1 to 3 µm) are introduced into the ATOFMS by vacuum through an aerodynamic lens that can focus and form a particle beam. Each particle has a size-dependent velocity which is determined by the time-of-flight between two orthogonal, continuous diode-pumped lasers. The firing of the desorption/ionization laser (Nd:YAG laser, 266 nm) is triggered when the particle enters the center region of the mass spectrometer. Both positive and negative ions generated from laser ablation are analyzed simultaneously. The power density of 266 nm laser was maintained at approximately $1.0 \times 10^8\,\mathrm{W\,cm^{-2}}$.

2.4 Analysis of filter samples using total organic carbon (TOC) analyzer, aerosol time-of-flight mass spectrometer (ATOFMS) and gas chromatography-mass spectrometer (GC-MS)

Particles (with diameters < 500 nm) generated from the drop-tube furnace were collected on quartz filters and then analyzed with a total organic carbon analyzer (TOC-LCPH Shimadzu Co.) for their total carbon content; and with a thermal/optical carbon analyzers (Model 2001, Atmoslytic Inc., Calabasas, CA) for the ratio of elemental carbon/organic carbon.

Particles collected on a quartz filter were also extracted by pure water in an ultrasonic bath. The extract was atomized to produce droplets. A diffusion dryer was used to dry the droplets. The dried aerosol was introduced into the ATOFMS and the mass spectra were obtained. Particles on a quartz filter were also extracted with 30 mL mixture of dichloromethane and methanol (3 : 1 in volume). Then the extract was filtered and concentrated to about 5 mL in a vacuum evaporator. A stream of ultrapure nitrogen was used to further concentrate the extract. Finally the extract was derivatized with BSTFA (BSTFA/TMCS, 99 : 1, Sigma-Aldrich Co.) and introduced into a GC-MS (Thermo ISQ GC-MS, Thermo Fisher Scientific Inc.) for analysis.

2.5 Ambient aerosol measurement in Shanghai

Ambient aerosol measurements were conducted in the laboratory building of the Department of Environmental Science and Engineering at Fudan University (31° 17′ 47.14″ N, 121° 30′ 14.94″ E) in Shanghai during two periods (22 ~ 28 December 2009 and 19 ~ 22 March 2010). This site is within an urban residential area that is impacted by traffic, construction emissions and other urban area sources. Ambient air was drawn from a height of approximately 5.5 m above the ground and about 0.5 m above the roof of the building through a half inch diameter 6 m long stainless steel tube at a flow rate of 6 LPM. A slip stream of air was analyzed by an ATOFMS. The ATOFMS data was imported to YAADA (version 2.0, http://www.yaada.org, Copyright Jonathan O. Allen 2008), a software toolkit for single particle data analysis written inMATLAB programming language (MATLAB, version 7.0). An adaptive resonance theory-based clustering method (ART-2a) was used to classify mass spectra (Song et al., 1999). Particles with sufficiently similar mass spectral patterns were manually merged into one class. The parameters used for ART-2a include a vigilance factor of 0.70, learning rate of 0.05 and 20 iterations. During the second sampling period (19 ~ 22 March 2010), a Monitor for Aerosols & Gas in Ambient Air (MARGA, Model ADI 2080, Applikon Analytical B.V.,

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the Netherlands) was used to determine ionic potassium concentrations in $PM_{2.5}$ of the ambient air. The detailed description of the field sampling using MARGA can be found in the literature (Du et al., 2011).

3 Results and discussion

The overall study examined the understanding of the pathways of organic aerosol formation by performing systematic experiments in a drop tube combustor. Using this information, the contribution of coal combustion sources to the ambient aerosol loading in Shanghai was established.

3.1 Characterization of organic aerosol from coal combustion in a drop-tube furnace

The average AMS organic mass spectra of the aerosol from the drop tube coal combustor under various oxygen/coal ratios, as shown in Fig. 2. Many significant organic peaks (such as *m/z* 43, 44, 55, 57, 60, 69, 73, 91) are observed, confirming that pulverized coal combustion produces organic aerosols, even at the high oxygen/coal ratios in the system (the oxygen/coal ratio is defined as "feed rate of O_2 in moles per hour/feed rate of carbon in moles per hour" and it ranged from 8.6 to 30.1; in combustion science, the equivalence ratio is commonly used, which is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio; here the equivalence ratios ranged from 0.12 to 0.033; in a coal-fired power plant the typical oxygen/coal ratio is 1.2). However, the fraction of organic matter to total fine particle mass is small. Inorganic compounds, such as SiO_2, CaO and Al_2O_3 are dominant species in coal combustion aerosol (Linak and Wendt, 1994) Figure S2 shows a unimodal particle size distribution from coal combustion. It also shows that changing oxygen/coal ratio did not significantly change particle size distributions.

The emission factors (EFs) of particulate matter, elemental carbon and organic carbon were also determined (Fig. 3a). These values are higher than the EFs that a previous study reported (Bond et al., 2004), since real coal-fired power plants use electrostatic precipitator or fabric filter baghouse to remove fine particulate matter. EFs of particulate matter from coal combustion are highly dependent on particulate emission control devices. In developed areas like North America, particulate emission is strictly regulated. Thus EFs of particulate matter from coal-fired power plants in these areas are very low. Therefore some studies showed that coal-fired power plants do not significantly contribute to primary organic aerosol emissions (Peltier et al., 2007; Zaveri et al., 2010). However, in developing areas with less pollutant control, EFs have very large uncertainties. The total carbon content in particulate matter in this case is about 13 %, which is in the range of the reported values for some industrial boilers (Zhang et al., 2008) The mass spectra in Fig. 2 are similar to those from biomass burning aerosols that were reported by Schneider et al. (2006). Particularly, peaks at *m/z* 60 and 73 are generally considered as important biomass burning particle tracers, since they result from fragmentation of levoglucosan, which is one of the major compounds emitted from biomass burning (Schneider et al., 2006; Weimer et al., 2008). To further characterize the organics, fine particulate matter from the coal combustor was collected on a quartz filter. The organics were extracted by a mixture of methanol and dichloromethane; derivatized with BSTFA and analysed by gas chromatography–mass spectrometry (GC/MS). No levoglucosan was detected (Fig. 3b), which implies that other detected compounds (e.g. some carboxylic acids) most likely contributed to the observed *m/z* 60 and 73. These masses have been previously observed with carboxylic acid samples in the AMS (Aiken et al., 2007). This observation implies that an ambient mass spectral signature with elevated *m/z* 60 and 73 could have biomass burning or coal combustion origins and supporting information should be explored to determine the major contributing source.

In the drop-tube coal combustion experiments, collected particles were also extracted with de-ionized water (18 MΩ), then atomized and measured by an Aerosol time-of-fight mass spectrometer (ATOFMS), which can analyse single aerosol particles by laser desorption/ionization (Gard et al., 1997). The ATOFMS mass spectrum (Fig. 3c) contains many inorganic peaks, such as Ca, Na and K. However, the K peak is comparatively low. This observation, however, is not consistent with the study by Suess et al. (2002) in which they observed larger K peaks in ATOFMS spectra for coal combustion particles in an in situ measurement (i.e. fresh emitted particles were directly introduced into ATOFMS and measured). The reason for the finding is that K has high mineral affinity (elements associated with aluminosilicates, carbonates and other minerals in coal ash), and only about 1 % of K in fly ash from coal combustion can be extracted by water (Querol et al., 1996). Peaks at *m/z* of −45, −59 and −73 in ATOFMS spectra are usually considered as the fragments of levoglucosan (Silva et al., 1999). These peaks detected in Fig. 3c are not from levoglucosan in this study; hence they are not unique biomass burning tracers for particles in the atmosphere. The similarity of the organic species in aerosol formed during coal combustion and biomass burning is due to the fact that coal has its origins from biomass and formed via coalification, which is a process that reduces hydrogen, oxygen content of biomass (with cellulose, lignin, hemicellulose being the major components) and increases the fraction of carbon content (Haenel, 1992)

3.2 Formation mechanisms of organic aerosol from coal combustion

OA formation is affected by oxygen/coal ratios. To examine this, the coal feed rate was changed while the air flow rate was fixed. Figure 2 contrasts mass spectra between higher oxygen/coal ratios (15.0 ~ 30.1) and lower oxygen/coal ratios (8.6 ~ 12.0). When the oxygen/coal ratio is lower than 12.0, the peak of CO_2^+ at *m/z* 44, an important indicator for oxygenated organic aerosols (OOA) (Canagaratna et al., 2007), becomes one of the dominant peaks in the mass spectrum, suggesting that OOA is a major component of particulate organic species. High-resolution AMS has the capability to determine elemental composition of organics (Aiken et al., 2008). At lower oxygen/coal ratio, the O/C molar ratios of the organic matter are around 0.25 (Fig. S3), which is similar to some fresh secondary organic aerosols generated in chamber experiments (Ng et al., 2010) Ion CO_2^+ is formed via the thermal decarboxylation of carboxylic acids (Aiken et al., 2007). Its presence suggests that many of the organic compounds in these mass spectra contain carboxyl functional groups and are highly oxygenated. Larger char particles were removed by the impactor as they have particle diameters larger than 1 µm. Therefore, the oxygenated organic matter should be formed from tar, which is composed of volatile products of coal pyrolysis. GC/MS measurement shows that the composition of the organics is mainly comprised of oxidized aromatic compounds and some fatty acids (Fig. 3b), which could be the oxidized tar compounds. At higher oxygen/coal ratio (> 15.0), abundance of the organic peaks is much lower, indicating OA formation is favored at lower oxygen/coal ratios.

Organic matter is typically fully oxidized (to gaseous CO_2 and CO) in air at high combustion temperatures. Thus, the organic matter detected in the particles was probably prevented from oxidation by unknown mechanisms in the combustor. A conjecture is proposed: the organic vapors are adsorbed by inorganic particles during coal combustion. After adsorption of organic vapors, inorganic particles may continue to grow, thereby covering and protecting organic matter from further oxidation. To test this hypothesis, different amounts of pure N_2 were added into the coal combustor to suppress inorganic particle formation (the mechanism has been explained by our previous study, Suriyawong et al., 2006). Formation of OA particles should be favored under fuel-rich conditions, which would be the case when more N_2 is added into the system as the oxygen/coal ratio is lowered. However, as shown in Fig. 4a, when more N_2 was added at a fixed coal feed rate of 3.0 $g\,h^{-1}$, organic peaks became significantly lower compared to the air case (lower nitrogen concentrations). Both the total particle number concentration and size became smaller, resulting in lower inorganic ash particle concentrations (Suriyawong et al., 2006). At the reduced overall inorganic particle concentrations, the surface area available for adsorption of organic vapor was also reduced (Fig. 4b). The similar phenomenon (Fig. S4) was also observed for the experiment with lower coal feed rate (1.0 $g\,h^{-1}$).

It could be hypothesized that decreased oxygen content is suppressing the oxidation of tar and thus suppressing formation of OA mass, however, Fig. 4c shows that the O/C ratio of particulate organic matter actually increases when the N_2/Air ratio increases, providing further support for the proposed mechanism where inorganic aerosol is protecting OA mass from further oxidation. Under lower additional-N_2/Air ratio, higher concentrations of inorganic particles are formed during coal combustion. With increased surface area, they adsorb more organic species, and prevent their further oxidation. Thus, the O/C ratio in the particulate matter is lower even under higher oxygen concentration (lower N_2/Air ratio), which is consistent with observations in Fig. 4c. In addition, size distributions of particles from coal combustion result in a maximum peak diameter at about 50 nm (Fig. S2). However organic mass size distributions peak at about 100 nm (Fig. S5), indicating organic matter is associated with the larger particles that have a higher surface area that provides better protection against oxidation

Figure 5 summarizes the proposed formation mechanisms of OA during pulverized coal combustion: molecules in coal usually contain aromatic clusters which are connected by hydrocarbon bridges and loops (Haenel, 1992). The bond strength of aromatic rings is much greater than those of the hydrocarbon bridges and loops. When coal particles are combusted in the furnace, bridges and loops break apart first. Tar, a group of compounds with smaller molecular weights, are released. In the furnace, most of gas-phase tar is quickly oxidized and fully combusted. However, some of the tar species are adsorbed by the inorganic ash particles with chemical composition such as SiO_2, Al_2O_3 CaO and sulfate. These particles can protect tar from further oxidation. Therefore, particulate organic matter survives the highly oxidizing environment, and may potentially be emitted to the atmosphere.

3.3 Identification of coal combustion aerosol in urban atmosphere

Combustion is a major source category contributor to the atmospheric aerosol (Bond et al., 2004). According to this study, particles from coal combustion are a mixture of inorganic and organic compounds and overlap with some well-known biomass burning tracers. Particles emitted from coal combustors have the potential to be incorrectly assigned as biomass burning aerosol by tracer-based source apportionment. This was demonstrated for the ambient aerosol sampled in Shanghai, China.

Ambient aerosol was measured in Shanghai using ATOFMS for two different periods (22 ~ 28 December 2009, 19 ~ 22 March 2010). ATOFMS can produce mass spectral signatures for single particles with diameters from 0.3 to 3 µm in ambient air. According to the similarity of the mass spectra, particles can be classified into several different types using ART-2a, a clustering algorithm (Song et al., 1999). As Fig. 6a shows, a unique type of particle is found, which accounts for 36 ~ 42 % of the total number of particles (Fig. 6b). It has dominant potassium (K^+, *m/z* 39) peaks in the positive spectrum and secondary inorganic peaks (NO_2^-, NO_3^-, HSO_4, etc.) in the negative spectrum. Li, Al, Ca, CaO/Fe and other metal/metal oxide peaks were also present. In addition, there are some organic peaks and elemental carbon peaks. Notably, CHO_2^- (*m/z* −45), $C_2H_3O_2$ (*m/z* −59) and $C_3H_5O_2^-$ (*m/z* −73) were found in the negative spectrum. Generally speaking, this mass spectral pattern is very similar to biomass burning aerosol that was identified in previous ATOFMS field studies (Moffet et al., 2008; Hatch et al., 2011). K^+, CHO_2^-, $C_2H_3O_2^-$ and $C_3H_5O_2^-$ peaks are considered as tracers for biomass burning aerosol in previous studies (Silva et al., 1999; Moffet et al., 2008).

However, this type of aerosol may not always be produced from biomass burning. Direct evidence is for this statement is provided in Fig. 7. One significant biomass burning source in/around Shanghai is the open field burning of crop straw, which usually occurs from May to June every year (Du et al., 2011). Water-soluble potassium is a good tracer for biomass burning aerosols (Gaudichet et al., 1995). Du et al. (2011) confirmed the presence of very high water-soluble particulate potassium concentrations (the mass faction was up to about 30 %) during the crop burning season (Fig. 7). However, the concentration of water-soluble K^+ in $PM_{2.5}$ was much lower in this study (shown in Fig. 7; the mass fraction was around 1 ~ 2 % during 19 ~ 22 March 2010), which suggests biomass burning aerosol was not the dominant aerosol type during this period; and the particle type shown in Fig. 6a (accounts for 36 ~ 42 % of the total number of particles). Furthermore, the land fire monitoring data from MODIS Rapid Response System (http://maps.geog.umd.edu) also clearly shows that no open fire was detected in Shanghai and its surrounding areas (Fig. 8) during the sampling period of this study. Moreover, according to the China energy statistical yearbook (National Bureau of Statistics of China, 2008), biomass is not listed as a major energy source for industrial or households in Shanghai. Therefore, there are very few biomass burning sources during the sampling periods; this particle type should be representative of a different source.

The ATOFMS (which can measure particles with sizes in the range between 0.3 to 3 µm) results show that about 40 % of particles contain very high potassium signals (Fig. 7). Since very low water-soluble potassium was observed, it strongly suggests that most of the potassium in the aerosol sampled in this study was not water-soluble. According to this study, K^+, CHO_2^-, $CH_3O_2^-$ and $C_3H_5O_2^-$ peaks can also be present in the ATOFMS spectra of particles from coal combustion. Potassium in coal combustion aerosol is not water-soluble (Querol et al., 1996). This leads us to conclude that the dominant type of aerosols during this study was very likely produced from coal combustion. Coal provided about 66 % of the total energy for Shanghai in 2008. Most coal is used for electricity generation and industry use (Fig. 9). Thus it is possible that coal combustion generates a significant amount of particulate matter that is released to the atmosphere because of the relatively loose regulation of air pollutant emissions in China (Chen et al., 2006). Domestic coal burning may also play a significant role in aerosol emission due to its higher emission factors (Zhang et al., 2008). Moreover, Shu et al.'s (2001) study also shows that coal combustion contributes 19.6 ~ 60.1 % of total suspended particle mass in Shanghai. Thus it is reasonable that this dominant aerosol type observed in the atmosphere was from coal combustion. Weaker peaks of Al, Ca, CaO/Fe shown in Fig. 6a may be due to the aging process of aerosols in the atmosphere: oxides of Al, Ca, Fe can quickly react with H_2SO_4 in atmosphere and form sulfates which have a much lower ionization efficiency in the ATOFMS (Middlebrook et al., 2003). Therefore, the Al, Ca, CaO/Fe peaks will be much weaker than those in freshly emitted particles.

4 Conclusions

Coal combustion produces fine particles with a fraction of carbonaceous matter (~ 13 % of total mass in this study), including both black carbon and organic carbon. It is shown from controlled bench scale pulverized coal combustion studies that inorganic aerosols play a critical role as carrier of organic species. Using some commonly-used aerosol mass spectrometry techniques (Aerodyne AMS, GC-MS and TSI ATOFMS), fine particulate matter from coal combustion was characterized in detail. The main OA components include oxidized aromatic matter and carboxylic acids. It was found that these organic species have similar mass spectra as those from biomass combustion aerosols. For atmospheric aerosol studies, due to the similarity of organic signals between coal combustion and biomass burning measured by both AMS and ATOFMS, some "biomass burning aerosol tracers" may not be reliable.

These coal combustor emitted particles can be a major atmospheric aerosol source in some regions such as Shanghai where coal combustion accounts for a large fraction of electricity generation. Ambient measurements in Shanghai, China, found the presence of some tracers, which were usually attributed to biomass burning, in 36 ~ 42 % of the sampled particles. With the absence of major biomass sources in the Shanghai area during the study period, it is suggested that coal combustion is probably the main source of these particles. This work shows that there is a significant potential for incorrect apportionment of coal combustion particles to biomass burning sources using widely adopted mass spectrometry techniques. The contribution of biomass burning aerosols may be overestimated if coal combustion systems are also present in the airshed. Therefore, it is critical to incorporate supporting information for the correct source apportionment of these particle types.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/13/3345/2013/ acpd-13-3345-2013-supplement.pdf.

Acknowledgements. This work was funded by the Consortium for Clean Coal Utilization at Washington University in St. Louis. Partial support by the National Natural Science Foundation of China (20937001) and the McDonnell Academy Global Energy and Environment Partnership (MAGEEP) are also acknowledged.

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Table 1. Summary of experimental conditions for drop-tube furnace study of pulverized coal combustion.

Set	#	O_2/Coal Ratio ($mol\,mol^{-1}$)	Coal Feed Rate ($g\,h^{-1}$)	Air Flow Rate (lpm)	Additional N_2 Flow Rate (lpm)	Air/ Additional-N_2 Ratio	Sampling Dilution Ratio	Objective
I	1	30.1	1	3	0	–	100.7	Organic aerosol formation under different O_2/Coal ratio
	2	20.1	1.5	3	0	–		
	3	15.0	2	3	0	–		
	4	12.0	2.5	3	0	–		
	5	10.0	3	3	0	–		
	6	8.6	3.5	3	0	–		
II	1	27.1	1	2.7	0.3	90/10	50.4	Organic aerosol formation under different gas compositions at lower coal feed rate ($1\,g\,h^{-1}$)
	2	24.1	1	2.4	0.6	80/20		
	3	18.1	1	1.8	1.2	60/40		
III	4	9.0	3	2.7	0.3	90/10	100.7	Organic aerosol formation under different gas compositions at higher coal feed rate ($3\,g\,h^{-1}$)
	5	8.0	3	2.4	0.6	80/20		
	6	6.0	3	1.8	1.2	60/40		

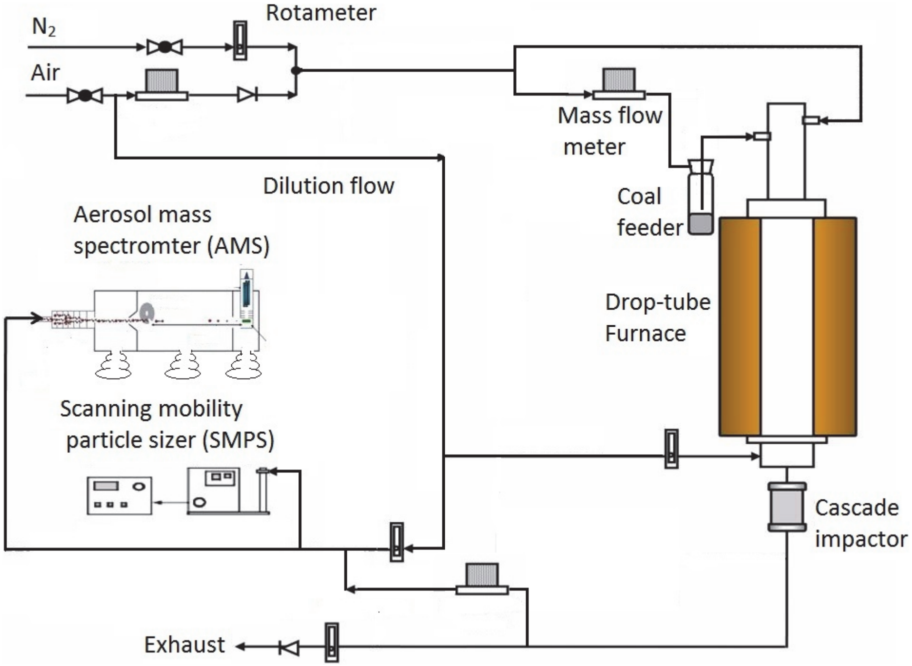


Fig. 1. Schematic drawing of the laboratory-scale pulverized coal combustion system with measurement instruments identified.

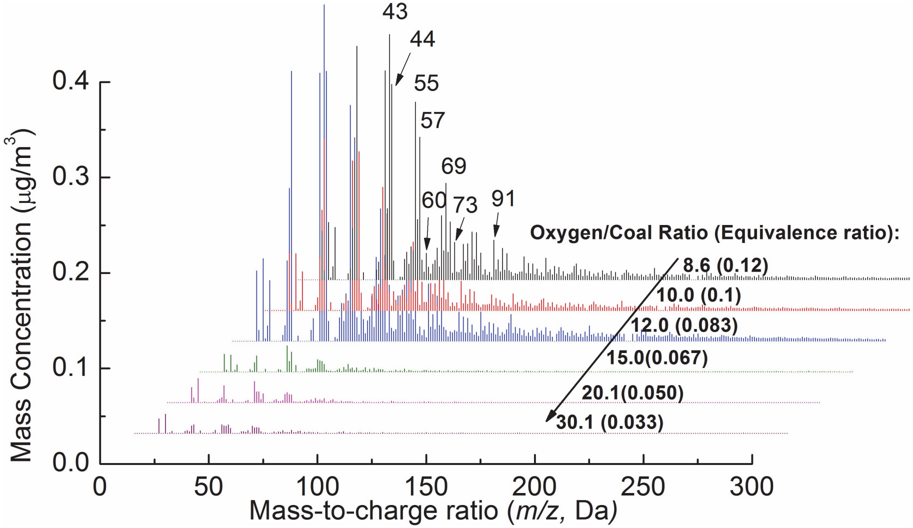


Fig. 2. Average organic mass spectra for fine particulate matter from pulverized coal combustion under different oxygen/coal ratios. Each mass spectrum corresponds to one oxygen/coal ratio. The mass spectra were obtained by an Aerodyne Aerosol Mass Spectrometer (AMS).

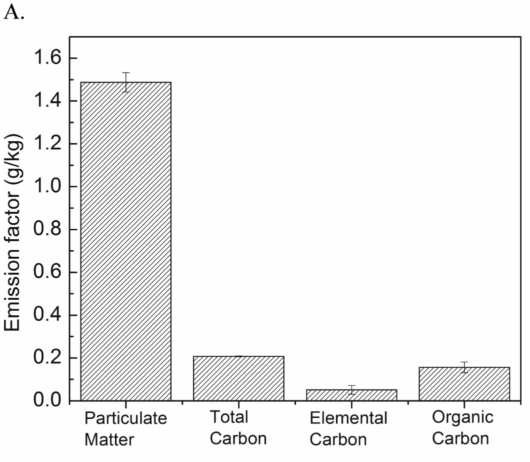


Fig. 3. **(A)** Emission factors of particulate matter, total carbon, elemental carbon and organic carbon from coal combustion. **(B)** GC-MS measurements of extracts from coal combustion particles. Different chemical compounds were separated depending on their retention time in GC column. Major compounds were identified according to their mass spectra: *A. Benzaldehyde, 3-methoxy-4-[(trimethylsiyl)oxy]-,O-methyloxime; B. 3-Hydroxybutyric acid, t-butyl ester; C. Benzaldehyde, 2-methyl-; D. 1,3-Benzenediol,o-(4-methylbenzoyl)-o'(2-methoxybenzoyl)-; E. Benzene, 1,3-bis(1,1-dimethylethyl)-; F. 2-Isopropyl-5-methyl-1-heptanol; G. Phenol,2,4-bis(1,1-dimethylethyl)-; H. Benzoic acid,3,5-bis(1,1-dimethylethyl)-4-hydroxy-,ethyl ester; I. 13-Docosen-1-ol,(Z)-; J. Hexadecanoic acid, methyl ester; K. n-Hexadecanoic acid; L. 14-Pentadecenoic acid; M. Oxtadecanoic acid, methyl ester; N. Oxtadecanoic acid*. The presence of some esters may be due to the derivatization of acids with BSTFA; **(C)** positive and negative mass spectra for extract of fine particulate matter from pulverized coal combustion. The mass spectra were obtained by an Aerosol Time-of-flight Mass Spectrometer (ATOFMS).

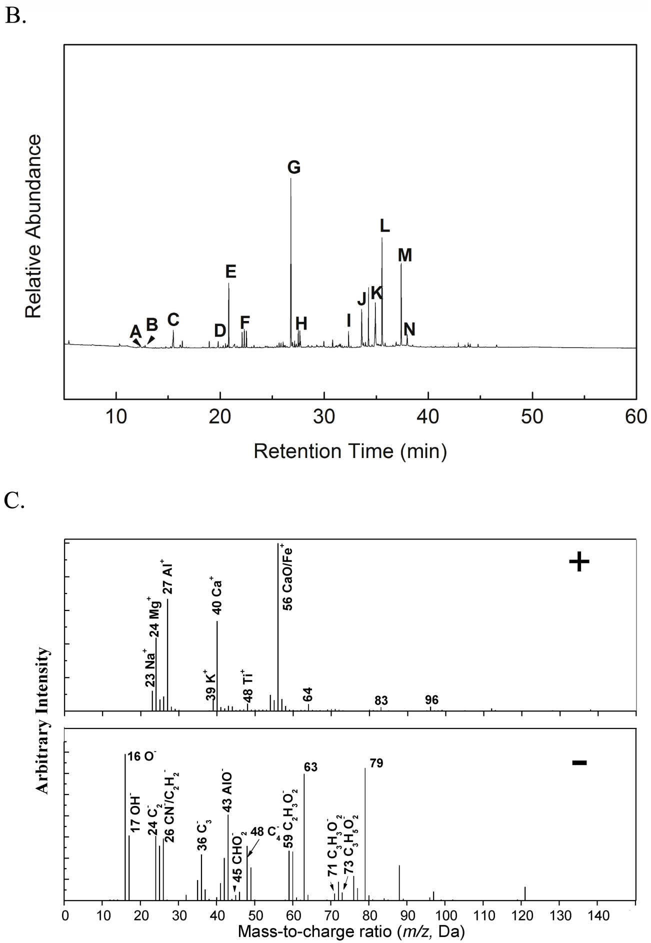


Fig. 3. Continued.

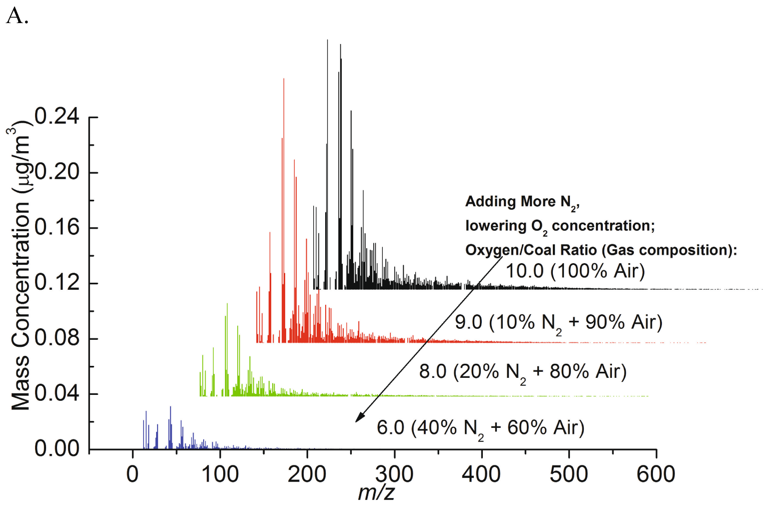
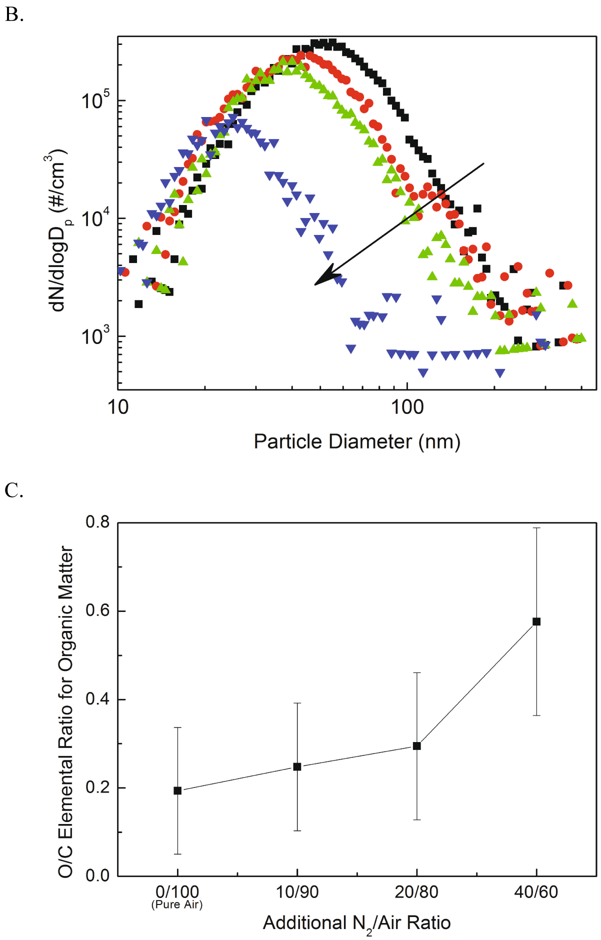


Fig. 4. **(A)** Average organic mass spectra and **(B)** size distributions for different additional-N_2/Air ratios while coal feed rate was fixed at $3.0\,\mathrm{g\,h^{-1}}$. The mass spectra were obtained by AMS. Each color of mass spectrum or size distribution corresponds to certain additional N_2/Air ratios: (Blank: Air; Red: 10 % N_2 + 90 % Air; Green: 20 % N_2 + 80 % Air; Blue: 40 % N_2 + 60 % Air); **(C)** Oxygen/Carbon (O/C) elemental ratios with error bars of organic matter for different additional-N_2/Air ratios.



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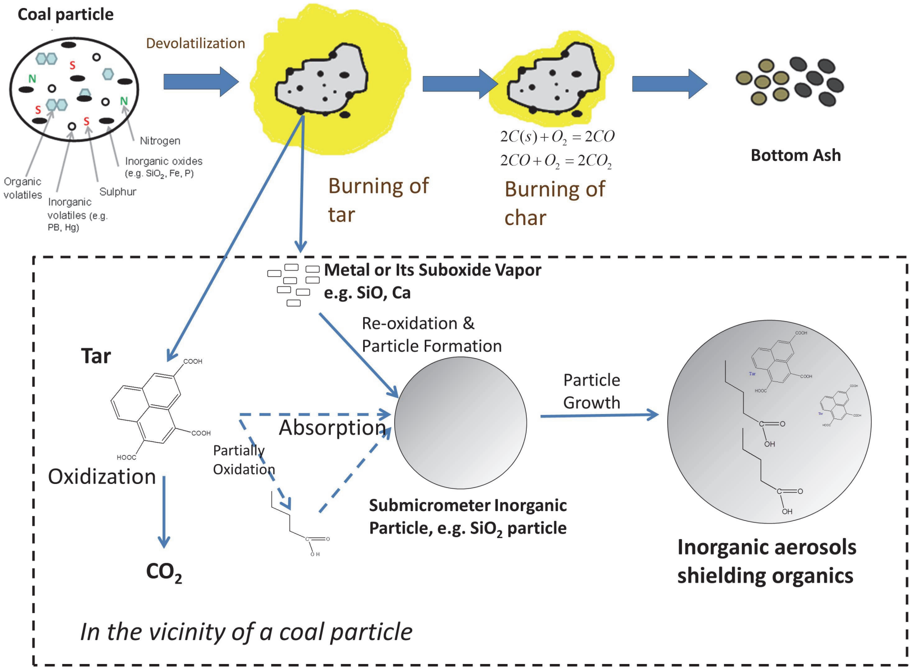

Fig. 5. Proposed formation mechanisms of OA from coal combustion.

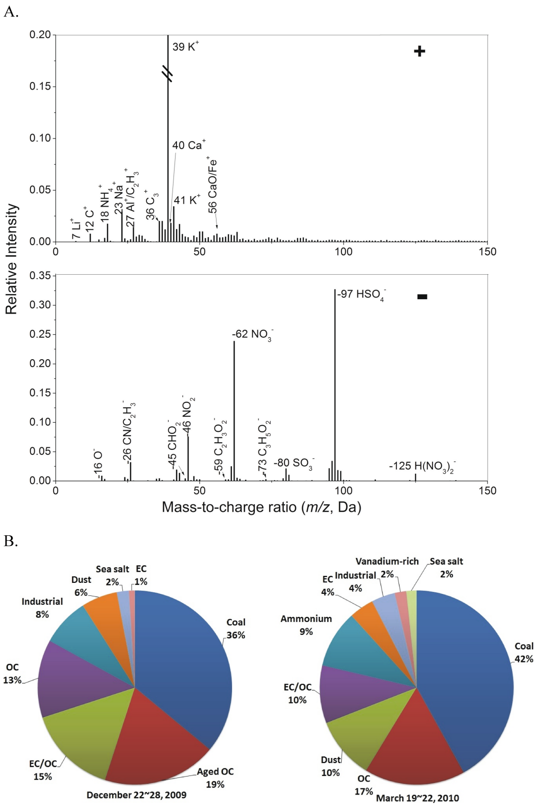

Fig. 6. (A) Average mass spectra of a dominant type of ambient aerosol in Shanghai using ATOFMS. The type of particles shown here are assigned as coal combustion particles. **(B)** Fraction of each particle type by number concentration during the sampling periods (22 ~ 28 December 2009 and 19 ~ 22 March, 2010). The particle type shown in Fig. 4a is assigned as "Coal", indicating that the particles in this category were most likely emitted from coal combustion.

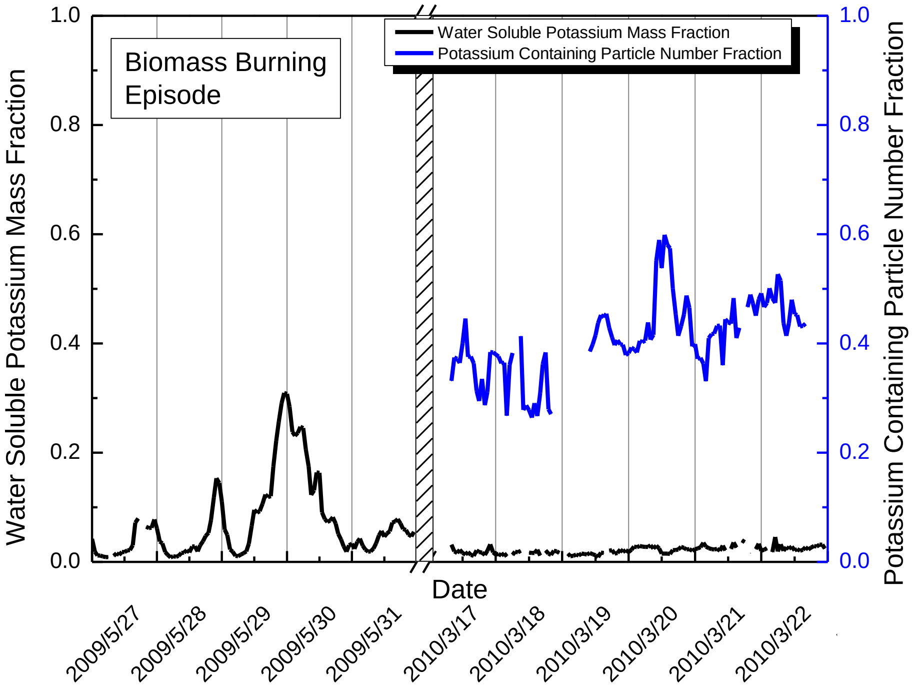

Fig. 7. Comparision of water-soluable potasium mass fraction and the number fraction of the aerosol type which is shown in Fig. 6a. The data for the biomass burning episode is adapted from Du et al. (2011).

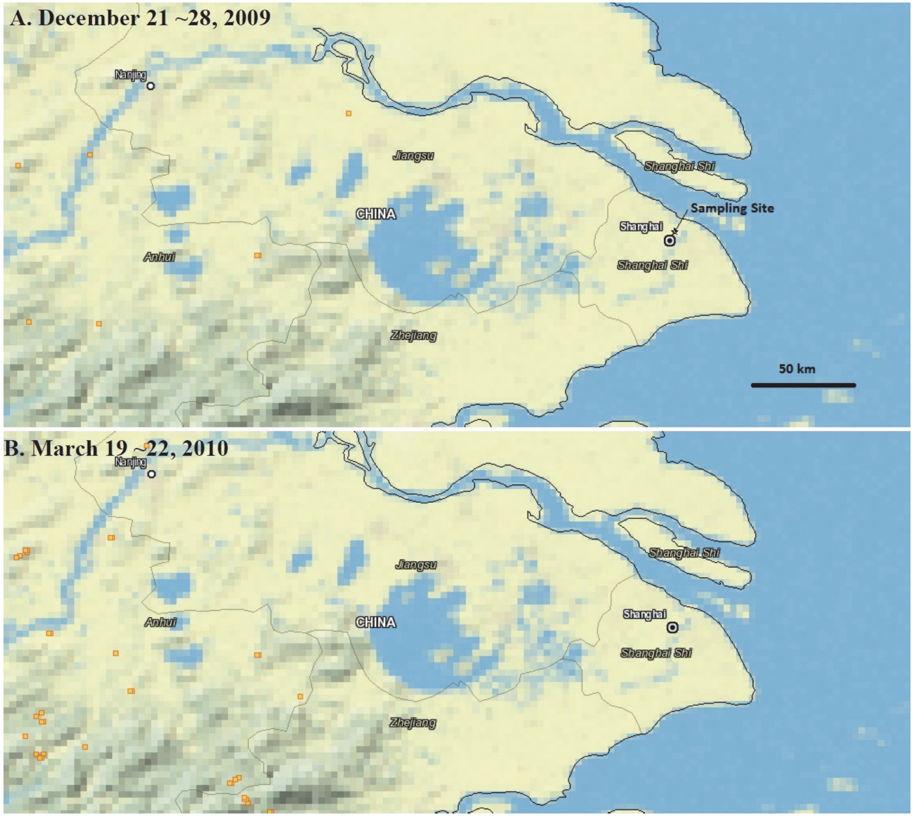

Fig. 8. Open fire event in/around Shanghai (Sampling site: 31° 17′47.14″ N, 121° 30′14.94″ E) during sampling periods. Each orange square represents a single fire event.

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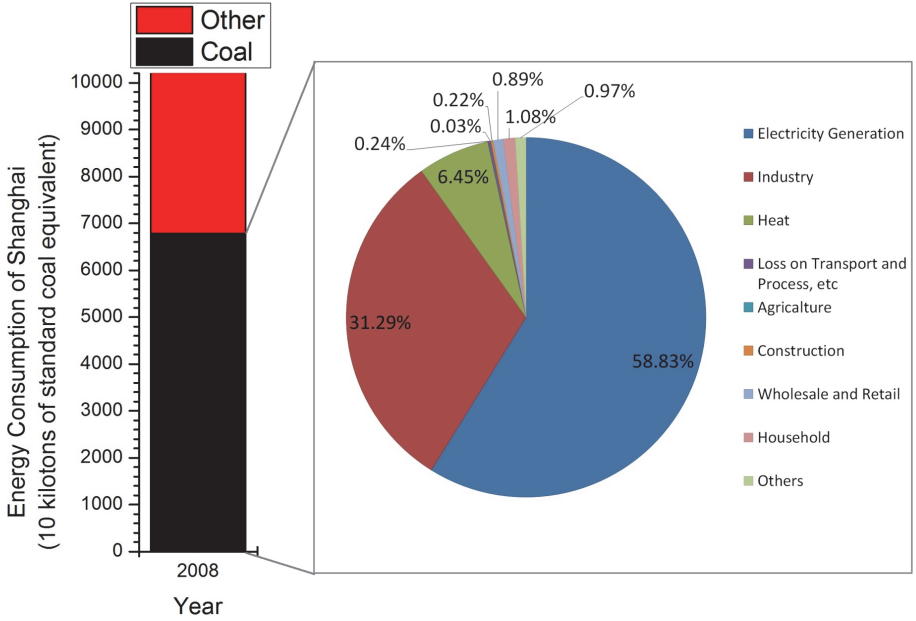

Fig. 9. Energy consumption in Shanghai during 2008. Coal combustion is the largest energy source. Breakdown by usage of coal is also shown. The data in this panel is adapted from referenced values (National Bureau of Statistics of China, 2008).