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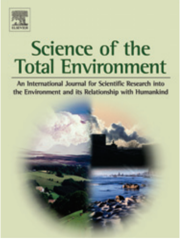

Semi-quantitative characterisation of ambient ultrafine aerosols resulting from emissions of coal fired power stations

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ABSTRACT

Emissions from coal fired power stations are known to be a significant anthropogenic source of fine atmospheric particles, both through direct primary emissions and secondary formation of sulfate and nitrate from emissions of gaseous precursors. However, there is relatively little information available in the literature regarding the contribution emissions make to the ambient aerosol, particularly in the ultrafine size range. In this study, the contribution of emissions to particles smaller than 0.3 μm in the ambient aerosol was examined at a sampling site 7 km from two large Australian coal fired power stations equipped with fabric filters. A novel approach was employed using conditional sampling based on sulfur dioxide (SO_2) as an indicator species, and a relatively new sampler, the TSI Nanometer Aerosol Sampler. Samples were collected on transmission electron microscope (TEM) grids and examined using a combination of TEM imaging and energy dispersive X-ray (EDX) analysis for qualitative chemical analysis. The ultrafine aerosol in low SO_2 conditions was dominated by diesel soot from vehicle emissions, while significant quantities of particles, which were unstable under the electron beam, were observed in the high SO_2 samples. The behaviour of these particles was consistent with literature accounts of sulfate and nitrate species, believed to have been derived from precursor emissions from the power stations. A significant carbon peak was noted in the residues from the evaporated particles, suggesting that some secondary organic aerosol formation may also have been catalysed by these acid seed particles. No primary particulate material was observed in the minus 0.3 μm fraction. The results of this study indicate the contribution of species more commonly associated with gas to particle conversion may be more significant than expected, even close to source.

1. Introduction

While the underlying toxicology remains contentious, it is now widely accepted that fine particles can have significant impacts on human health (WHO, 2003). Coal fired power stations are a significant anthropogenic source of these fine particles, and power station emissions have received considerable attention as they are associated with a number of features of fine particle pollution which may contribute to health effects. These include heavy metals, acidic aerosols and ultrafine particulates (Kauppinen and Pakkanen, 1990; Querol et al., 1999; Lighty et al., 2000; Nelson, 2007).

A large number of previous studies have been conducted both on the characterisation of emissions and their impact on the ambient aerosol (Lighty et al., 2000). Much of the early work concentrated on either the visibility impacts of the

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Table 1 – Annual emissions (kg) from Bayswater and Liddell Power Stations for 2002/2003 reporting year (NPI, 2004)

Station	Stack Height	PM_{10} Emissions	SO_x Emissions	H_2SO_4 Emissions	NO_x Emissions
Bayswater	250 m	380,000	83,000,000	930,000	39,000,000
Liddell	168 m	290,000	36,000,000	370,000	18,000,000
Combined		570,000	119,000,000	1,300,000	57,000,000

Note: SO_3 emissions are reported as H_2SO_4 equivalent.

gaseous emissions (Friedlander, 1977), or the enrichment of trace and potentially toxic elements in the fine size fractions of the particulate emissions (Linton et al., 1976). Detailed elemental analyses and statistical techniques have been widely used to identify and quantify the contribution of a "coal combustion" source to the ambient particle concentrations (Dzubay and Mamane, 1989; Cohen et al., 1996; Begum et al., 2005). However, these estimates require further qualitative and quantitative examination using a range of analytical techniques, especially for the very fine particle sizes.

The efficiency of modern emission control systems is such that the contribution of indirect particulate matter formed through the oxidation of gaseous precursors in the emissions can be more significant than the primary particulate emissions (Querol et al., 1999). A number of studies have assessed the contribution of sulfate aerosol in the vicinity of power stations (Querol et al., 1998). There has been relatively little work conducted in Australia, although sphagnum moss has been used to show that the contribution of coal fired power station emissions to trace element concentrations in the vicinity of the stations is relatively minor (Swaine, 1994).

This paper details the results of investigations of ultrafine particles undertaken as part of a more extensive project which assessed the contribution of power station emissions to the ambient aerosol at a near source sampling site (Hinkley, 2005). Three distinct sampling and analysis approaches were employed in the study. The plus 1 μm material was collected with a Burkard spore sampler and analysed with Scanning Electron Microscopy, while the minus 1 plus 0.3 μm material was collected in size fractions using a cascade impactor, and assessed using Ion Beam Analysis and principal component analysis (Hinkley, 2005; Hinkley et al., in preparation). The minus 0.3 μm particles were collected using a relatively novel aerosol sampler – the TSI Nanometer Aerosol Sampler (NAS) – and analysed using Transmission Electron Microscopy (TEM) with Energy Dispersive X-Ray analysis (EDX).

Sampling was conducted in the Upper Hunter Valley of the state of New South Wales (NSW) near two large, modern coal fired power stations. Conditional sampling using SO_2 as an indicator species for probable plume presence was adopted to investigate the contribution of power station emissions to the ambient aerosol.

2. Methodology

2.1. Location of study site

The Upper Hunter region of NSW is a major energy producer and exporter. The region has numerous coal mines (predominantly open-cut) and two large coal fired power stations — Bayswater and Liddell. These stations have a combined capacity of around 4.6 GW and account for around 40% of the electricity produced in NSW (DUAP, 1997). Both stations are equipped with fabric filters for particulate emission control. The fuel used at the power stations is relatively low in sulfur, averaging around 0.65% sulfur, and stack emissions are not scrubbed for acid gas removal. Stack emissions are dependent on load and fuel quality but average around 8 mg m^{-3} of total suspended particulates, 450 ppm oxides of sulfur (SO_x) and 300 ppm oxides of nitrogen (NO_x) (Hinkley, 2005). Table 1 summarises reported emissions for the two stations (NPI, 2004).

The power stations are located between the townships of Singleton and Muswellbrook, and are approximately 20 km to the south east and 15 km to the north west of the stations respectively. The site is approximately 100 km from the eastern coast of Australia. The Hunter Valley is a wide, relatively shallow basin approximately 15 km wide at this point, which spreads out as it approaches the coast. Meteorology is characterised by low level inversions and local airflows up and down the valley from the SE and NW respectively (Bridgman and McManus, 2000). Overnight drainage flows of 3–4 m s^{-1} often persist into the early or late afternoon, with sea breezes more prevalent in summer (Bridgman and McManus, 2000).

An existing air pollution monitoring site at Ravensworth was selected for the field sampling after reviewing historical data from a number of monitoring sites in the area and examining the results of dispersion modelling (Hinkley, 2005). The monitoring site ("R") is approximately 7 km to the south east of the power stations ("L" and "B") as shown in Fig. 1. The site is approximately 50 m from the New England Highway, one of the principal roads in the area, and a railway line passes approximately 160 m to the east.

2.2. *Conditional sampling methodology*

The validity of SO_2 as an indicator species for the presence of the plume was investigated by exploring historical gas monitoring data from the Ravensworth site provided by Macquarie Generation. As shown in Table 1, the stations are substantial emitters of both SO_x and NO_x, but it was unknown whether other local sources were likely to influence the SO_2 concentrations observed at Ravensworth.

Fig. 2 shows a plot of SO_2 versus NO_x concentrations at the Ravensworth monitoring site. Two broad groups of data are evident in the plot — a first group where SO_2 and NO_x are strongly interlinked, and a second group where NO_x is apparently independent of SO_2. The first group is interpreted as resulting from the power stations emissions, while the