SEASONAL VARIATIONS IN SIZE-RESOLVED CHEMISTRY AND AEROSOL OPTICAL PROPERTIES IN SYDNEY, AUSTRALIA.

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Abstract

In recent years it has become evident that size resolved chemical composition of atmospheric aerosols is important in determining optical properties such as refractive index, scattering and absorption coefficients, extinction and hygroscopicity. These properties affect the way radiation is scattered and absorbed as it passes through the atmosphere, and thus are important for the calculation of aerosol radiative forcing and "atmospheric correction" of satellite images, as well as local air quality and visibility.

Here we report some preliminary results from a study of the size-resolved chemistry of atmospheric aerosols and their relationship to optical properties, which is currently under way in Sydney. The aim is to measure chemistry (PM2.5 and PM10 in this case) and optical properties (scattering coefficient) at a number of different sites around Sydney, at different times of the year, in order to determine the spatial and temporal variations. Samples are analysed using Ion Beam Analysis (IBA) and Scanning Electron Microscopy. The data collected will then be used to build an optical model of Sydney aerosols.

Samples were collected at four sites during the summer, autumn, winter and spring of 2003. These have been analysed using Ion Beam Analysis (IBA) and selected samples have also been analysed by Scanning Electron Microscopy (SEM). Seasonal and spatial variations in the chemical composition of 24-hour aerosol samples, and the simultaneous nephelometer measurements (hourly averages) will be presented. Early indications from IBA show seasonal differences within sites and between sites, as well as differences, in at least some cases, between PM2.5 and PM10 composition at particular sites. Seasonal and spatial differences have also been noted in the nephelometer measurements.

Keywords: Aerosols, Aerosol chemistry, Aerosol optical properties

1. Introduction

Atmospheric aerosols are among the most heterogeneous of the Earth's atmospheric components. Primary aerosols are injected directly into the atmosphere (e.g. desert dust, sea spray, smoke particles), while secondary aerosols are produced by gas-to-particle conversion of precursor gases such as SO_2 and biogenic compounds. Each may be the result of either natural or anthropogenic processes. Once in the atmosphere they may undergo further processing, especially within cloud droplets, leading to further changes in characteristics. Hence it is not just the concentrations, or column "loadings", of aerosols, but also the properties of the aerosol populations themselves that vary in space and time.

Aerosol properties include the size distribution, chemical composition, hygroscopicity (a measure of aerosol growth due to humidity), and refractive index as a function of both size and wavelength. Their optical properties such as extinction, scattering and absorption coefficients, and single scattering albedo (ratio of scattering to scattering plus absorption) depend on refractive index and size. In turn, refractive index depends on chemistry. All of these properties will vary with time and location. These characteristics are needed in order to construct the aerosol models used in a range of environmental (and other) applications.

Atmospheric aerosols are known to influence the Earth's climate, at both global and regional scales, via a number of mechanisms. Aerosols may scatter sunlight back to space, leading to a planetary cooling, or negative 'radiative forcing' – a process known as the direct aerosol forcing mechanism (Charlson 1992). Carbonaceous aerosols are highly absorbing of sunlight – a process known as the semi-direct mechanism. While both of these mechanisms reduce solar radiation at the surface, with obvious agricultural implications, the semi-direct mechanism also leads to a local atmospheric heating. This may lead to changes in atmospheric vertical stability, and even influence weather patterns (Ramanathan 2001).

Many types of aerosols are hygroscopic, and may act as cloud condensation nuclei. Thus, an increase in the concentration of such aerosols leads to an increase in the number of cloud droplets for the same total cloud liquid water content – that is, more, but smaller, droplets. This has two consequences. Firstly, such clouds tend to be more reflective, and hence act to cool the planet (Kaufman & Fraser 1997). Secondly, such clouds tend to survive longer before drizzle formation, which also implies a planetary cooling. These two processes are known as the first and second indirect mechanisms (Houghton 2001, Penner et al. 2004).

At the local and regional level, there are well-established statistical connections between high particulate levels and a number of health problems (Jacobson 2002). These concerns about the health effects of aerosols have led to the proposal to introduce a national air quality standard for “particulate matter” less than 2.5 μm diameter (known as PM2.5), in addition to the existing standard for PM10 – particles less than 10 μm diameter. The reason for this concern is that smaller particles have a much greater chance of reaching the lungs.

Atmospheric aerosols are the primary cause of the reduction in visibility which occurs in “hazy” environments, and are also of concern at a number of locations of outstanding scenic beauty in the USA, where several monitoring networks have been established (Jacobson 2002). This reduction in atmospheric transparency also impacts on satellite observation of the Earth’s surface, so that "atmospheric correction" to such imagery is required.

Around the world, aerosols and their effects are being studied by a variety of approaches. A series of intensive field campaigns has been conducted over the past decade, to study the physical, chemical and radiative effects of aerosols, primarily in order to better understand their climatic impacts (e. g. Raes et al. 2000). Long term monitoring is carried out from selected sites, such as those of NASA’s Aerosol Robotic Network, to which CSIRO also contributes (Holben et al. 1998). Local and regional air quality is being monitored to varying degrees in many locations including Sydney. Satellite observations are also used to infer global and regional properties of aerosols, such as air quality and climate forcing, but to do this a model, which must assume certain aerosol physical, chemical and optical properties, is needed (Kaufman, 2002). Similarly, aerosol optical models are used in radiative transfer codes which calculate aerosol climate forcing (Charlson 1992, Houghton et al., 2001). Finally, atmospheric haziness affects UV radiation at the surface, and must be included in daily forecasts of the UV index. In these and other applications the accuracy of the final result depends in large part on the accuracy of the assumed aerosol model (Twomey 1996, Kaufman & Tanre 1996).

The importance of size-resolved chemical composition in determining aerosol properties has become more evident in recent years. In Australia there have been a number of studies which have looked at the chemical composition of aerosols and their effects (e.g. ERDC 1992, Cohen et al. 1996, Ayers et al. 1999, Iinuma et al 2000). Previous work carried out by our group has made use of available chemical composition data to investigate the relationship between chemical composition and aerosol optical properties, to model aerosol hygroscopicity, and to calculate aerosol radiative forcing for Sydney (Iinuma 2000, Taha 2000, Box et al 2002). The current project will build on this work. We aim to characterize the physics, chemistry and optics of Sydney aerosols as a function of particle size and thus develop a model which can be used in a wide variety of environmental applications.

2. Methodology

2.1 Sampling

Approximately 100 aerosol samples were collected on 47mm Whatman Nuclepore polycarbonate filters between December 2002 and December 2003. The samples were collected using two Ecotech MicroVol samplers, a PM2.5 and a PM10, and sampling time was 24 hours. Four sites were used in the current sampling program: University of New South Wales, Campbelltown, Berrima and Moss Vale. The University of New South Wales is in an urban area close to the coast and the centre of Sydney, Campbelltown is a semi-urban area about 50 km southwest of the city centre. Berrima and Moss Vale are rural areas in the Southern Highlands just south of the Sydney Basin. In order to investigate both seasonal and spatial variability, each site was sampled for several days on at least four occasions throughout the year to collect data representative of summer, autumn, winter and spring. A Radiance Research M903 Integrating nephelometer was run alongside the two samplers to provide a continuous measurement of the aerosol scattering coefficient. Further samples may be taken in the future, depending on the results obtained from the existing data set.

2.2 Sample Analysis

Several techniques have been used to analyse the aerosol samples. Each sample was weighed before and after exposure. The elemental composition of the samples was determined using Ion Beam Analysis (IBA) and elemental carbon was determined using the Laser Integrating Plate Method (LIPM) at ANSTO. Accelerator based IBA is ideal for analysing aerosol samples because it is rapid, non-destructive and can detect low concentrations. The elements which can be detected using these analyses are Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, Br, Pb, Na, Li, B, and F (Cohen 1998).

Selected samples have also been analysed using a Scanning Electron Microscope at UNSW. The primary aim of SEM analyses is to obtain information about particle size and shape, and individual particles, however some information about elemental composition is also obtained.

2.3 Data Reduction and Optical Model

The chemical composition information obtained from the IBA analysis, along with environmental data such as temperature and pressure, will be used as input for a chemical thermodynamic model. This chemical thermodynamic model will use the input data to determine the aerosol species present in the atmosphere at the time of sample collection. Having determined the species present, refractive index will then be determined using the partial molar refraction approach and values of refractive index for various species from the literature. Size information from SEM analyses, along with the determined refract index, will then be used as input to a Mie code to calculate the aerosol scattering coefficient for the PM2.5 samples. The calculated scattering coefficient will be compared with nephelometer measurements in order to get an estimate of the accuracy of the optical model.

3. Preliminary Results

3.1 Aerosol Loading

Table 1 gives the average mass loading each season for three sites. As can be seen from the Table, the aerosol mass loading is higher in the summer for all sites. As would be expected for a rural area, Moss Vale has the lowest mass loading.

Table 1: Aerosol Loading (μgm^{-3})

	UNSW		Campbelltown		Moss Vale	
PM	2.5	10	2.5	10	2.5	10
Summer	9.3	52.8	11.6	41.2	2.7	9.9
Autumn	3.9	18.1	3.1	5.0	1.9	5.1
Winter	3.6	5.4	3.8	6.4	2.2	3.6
Spring	2.7	4.7	2.3	4.0	2.2	3.0

When the ratio of PM2.5 values to PM10 values are compared across the sites we find that for UNSW PM2.5 is around 20% of the PM10 value in summer and autumn, rising to 60 - 65% in winter and spring. For Campbelltown PM2.5 is around 30% of the PM10 value in summer, rising to around 60% for the other seasons. For Moss Vale the PM2.5 value is around 30% of the PM10 value in summer and rises steadily to 70% in spring. Thus it appears that there are seasonal and spatial variations in mass loadings of both fine and coarse particles in the Sydney region.

The results for the fourth site, Berrima, also showed lower mass loadings than the urban sites, with the highest loading in the summer. In summer the PM2.5 value was around 70% of the PM10 value, and for the other seasons it ranged from 35 - 50%. The results for Berrima may be influenced by the presence of a concrete plant nearby.

3.2 Chemical Composition

Analysis of the elemental composition, including elemental carbon, reveals that there are seasonal differences within sites as well as between sites. In order to identify the differences in chemical composition of the fine particles (PM2.5) and the coarser particles, the PM2.5 results were subtracted from the corresponding PM10 results to give a PM10-PM2.5 fraction. The most abundant elements were sodium, chlorine, elemental carbon, sulphur, silicon, aluminium, iron and fluorine. The proportion of these elements as a percentage of total deposited mass showed variations between sites, with size fraction and with season.

Figure 1 shows the average concentration, as a percentage of total deposited mass, of the most common elements for all four sites in the summer. The top panel is for the PM2.5 samples while the bottom panel shows the PM10-PM2.5 fraction. The differences between the sites, and between size fractions are noticeable. For all sites except Berrima, elemental carbon concentrations are higher in the PM2.5 fraction than in the coarse fraction, as might be expected if the main source was motor vehicle emissions. There also is some spatial variation in the PM2.5 elemental carbon concentrations.

Another interesting feature is the differences in sodium and chlorine, especially the small proportions of chlorine at Moss Vale and Berrima compared to UNSW and Campbelltown. This variation in proportions of sodium and chlorine also showed seasonal variations. As was noted above, the results for Berrima may be influenced by a nearby concrete plant.

Most of the other elements are present in very small concentrations making it difficult to draw strong conclusions about differences between sites or size fractions. However silicon is more evident in the PM10-PM2.5 fraction, and at UNSW and Campbelltown. Sulphur, on the other hand, is more evident in the PM2.5 fraction.

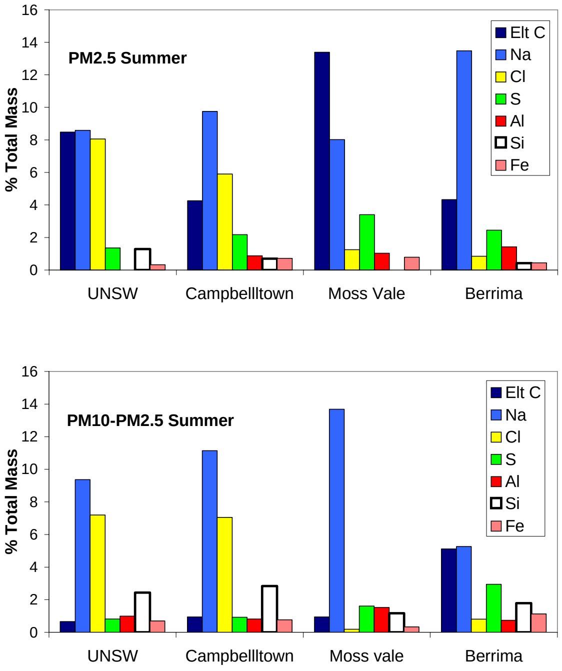

Figure 1. Spatial variation in aerosol composition. for summer

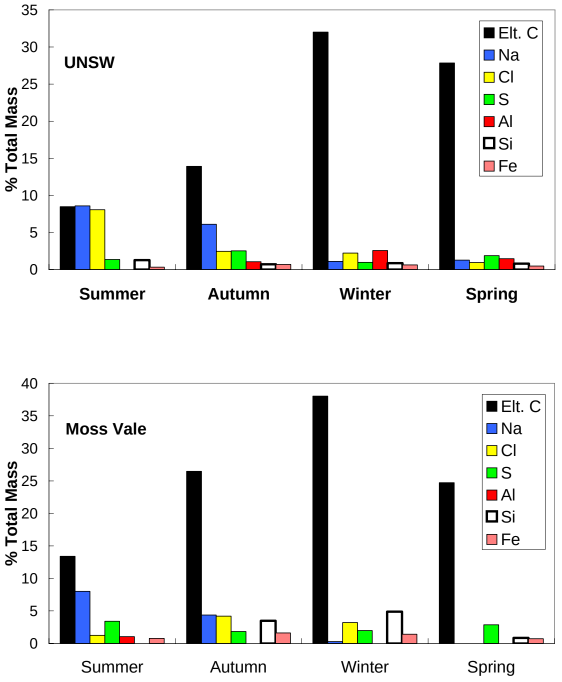

Figure 2. Seasonal variation in PM2.5 aerosol composition

The top panel in Figure 2 shows the seasonal variations in composition of PM2.5 aerosols for UNSW while the lower panel shows the variations for Moss Vale. At both sites the elemental carbon is lowest in summer, rises to a maximum and drops slightly in spring. At both sites there are seasonal variations in the relative proportions of sodium and chlorine, there are also marked differences in the proportions of these elements between the two sites. This probably reflects their different locations. Sulphur, silicon and aluminium all show seasonal variations, and the patterns of variation are different at the two sites. Silicon is most evident in autumn and winter at Moss Vale, but is present at very low concentrations throughout the year at UNSW. Aluminium on the other hand is present in the UNSW samples but not in the Moss Vale samples. The statistical significance of the variations in composition is currently being investigated.

3.3 Other Results and Further Work

Preliminary analysis of the nephelometer data has shown spatial and seasonal variations in scattering coefficient. These have not been analysed in detail at this stage but appear to be consistent with the aerosol mass concentrations measured. The nephelometer results will also be used to gauge the variability of PM2.5 aerosol concentration throughout the sampling period. Work is currently under way to investigate correlations between meteorological parameters such as wind speed and direction and aerosol chemistry and hence sources. At Berrima, for example, the aerosol chemistry will be affected by the presence of a cement works in the area. While SEM has been done on samples, these results have not yet been analysed.

The next phase, after completion of data reduction of IBA analyses, will be to use the thermodynamic model to determine the aerosol species present. The procedure used for this phase will be that used by Iinuma (2000, 2001). Aerosol refractive index will then be determined by the molar refraction approach, using chemical species determined from elemental composition, and refractive index values from the literature. Nephelometer data will be used to help determine the accuracy of these values.

4. Summary and Conclusions

The results obtained to date show that there are clear seasonal and spatial variations in the composition of aerosols in the Sydney region. There are also variations in composition of fine and coarser particles, which may result in variations in optical properties according to size.

Work is currently under way to determine the statistical significance of differences in aerosol chemistry, and also to relate these to factors such as meteorological conditions. Also yet to be done is the thermodynamic modelling and subsequent development of an optical model for Sydney.

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