

SIZE-RESOLVED PROPERTIES OF SYDNEY URBAN AEROSOLS

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1. INTRODUCTION

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. Due to their inherent spatial and temporal variability, it is essential to monitor aerosol physical, chemical and optical properties at as many locations as possible, in order to build up a comprehensive understanding of aerosols and their potential environmental impacts.

The size-resolved chemical composition of atmospheric aerosols is important in determining optical properties, such as refractive index, which 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. Since small particles can easily penetrate the lungs, such information is also important for air quality and health.

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). Hallal (2007) used a low volume PM_{2.5} and a low volume PM₁₀ sampler to study of the size-resolved chemical composition of aerosols in the Sydney region during 2003. The aim of that study was to determine the existence of the seasonal and spatial variations in aerosol chemistry and optical properties of the sites included in the study.

In the current study samples were collected using Micro Orifice Uniform Deposit Impactor (MOUDI), which divides the samples into 12 size fractions between 0.056 and 18 μm in aerodynamic diameter. Elemental chemical composition of the samples was determined using Ion Beam Analysis (IBA). The finer size-resolution will allow better characterization of the aerosol properties. Two sites are compared, Merrylands in

the western suburbs of Sydney and UNSW campus which is close to the coast and the Sydney CBD.

2. METHODOLOGY

2.1 Sampling

Measurements were taken at each site at several times throughout the year in order to determine seasonal and spatial variations in aerosol properties. The results reported here represent one measurement at each site during the months of April, May, June, July and August. Wind speed and direction were also recorded.

The MOUDI was run for 12 hours during each sampling run, and samples collected on 47mm polycarbonate Poretics filters, except for the final stage where a Teflon-backed Fluoropore filter was used. The MOUDI is a cascade impactor designed for a flow rate of 30L/min. The cut points for the stages are 18, 10, 5.6, 3.2, 1.8, 1, 0.56, 0.32, 0.18, 0.1 and 0.056 μm . The flow rate, start and finish time were recorded to allow calculation of total volume so that mass concentrations could be calculated.

2.2 Chemical analysis

All sample filters were weighed before and after sampling, and the mass deposited determined by subtraction. Samples were also measured before and after sampling using the Laser Integrating Plate Method in order to determine elemental carbon, although these results will not be discussed here.

Elemental composition of each filter was determined at the Australian Nuclear Science and Technology Organisation (ANSTO) Ion Beam Analysis facility at Lucas Heights. Accelerator based ion beam analysis techniques have been proven to be an ideal techniques for elemental analysis of aerosols. They are fast, non-destructive techniques that require no sample preparation which means samples can be used again by other different techniques (Cohen 1998; Cohen et al. 2004).

Particle Induced X-ray Emission (PIXE) was used to determine the elements Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Mg, Fe, Co, Cu, V, Ni, Zn, Br, Sr, Se, and Pb simultaneously from a few ng/m^3 upwards. Particle Induced Gamma ray Emission (PIGE) is useful for the analysis of light

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	April	May	June	July	August	Average
Merrylands						
PM1	38.2	34.3	23.7	59.4	72.9	38.7
PM2.5	54.3	44.6	34.5	75.3	92.5	60.2
PM10	77.8	59.2	49.7	99.7	127.5	82.8
TSP	105.5	71.4	63.8	112.3	149.3	100.5
PM2.5/TSP	51%	62%	54%	67%	62%	59.2%
PM1/PM2.5	70%	77%	69%	79%	79%	74.8%
PM1/TSP	36%	48%	37%	53%	49%	44.6%
UNSW						
PM1	28.0	10.6	30.5	14.3	18.7	20.4
PM2.5	38.1	13.8	37.5	17.7	22.5	25.9
PM10	51.7	20.9	48.2	24.4	29.1	34.9
TSP	63.8	26.6	53.3	29.3	32.7	41.1
PM2.5/TSP	60%	52%	70%	61%	69%	62.4%
PM1/PM2.5	73%	77%	81%	80%	83%	78.8%
PM1/TSP	44%	40%	57%	49%	57%	49.4%

Table 1. Mass concentrations in $\mu\text{g}/\text{m}^3$ and ratios of size fractions for all sampling days

elements such as Li, B, F, and Na. The elemental composition results are returned as $\mu\text{g}/\text{cm}^2$ which must then be converted to $\mu\text{g}/\text{m}^3$ if volume concentrations are needed.

3. PRELIMINARY RESULTS

3.1 Mass Concentrations

The mass concentrations from the twelve MOUDI stages were inverted using a program developed at CSIRO to obtain a smoother size distribution. The program is based on the efficient non-linear iterative procedure outlined by Twomey and Zalabsky (1981). The inversion results were then used to determine PM1 (particle mass < 1 μm), PM2.5, PM10 and TSP (total suspended particulate) for each sample. T results, along with ratios are shown in Table 1.

It can be seen from Table 1 that there is some variability in mass concentrations across the sampling period for both Merrylands and UNSW, with the UNSW concentrations generally being lower than those for Merrylands although the average ratios of the size fractions are much the same for both sites. For both sites the PM1 fraction accounts for a significant percentage of the total mass, ranging from 40% to 60%. PM1 also accounts for most of the PM2.5 fraction. It is these fine fractions which have the most impact on health.

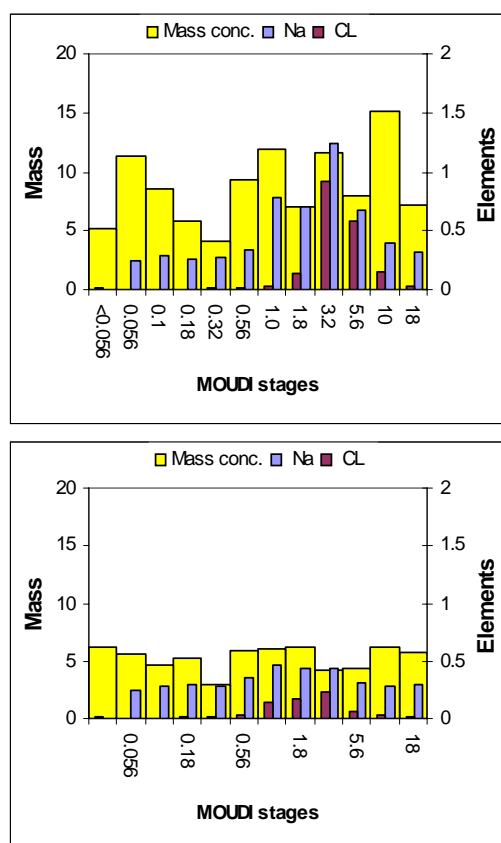


Figure 1. Comparison of mass concentrations ($\mu\text{g}/\text{m}^3$) and elemental concentrations ($\mu\text{g}/\text{cm}^2$) for sodium and chlorine as a function of size for April 2008. The top plot is for Merrylands and the bottom one is UNSW.

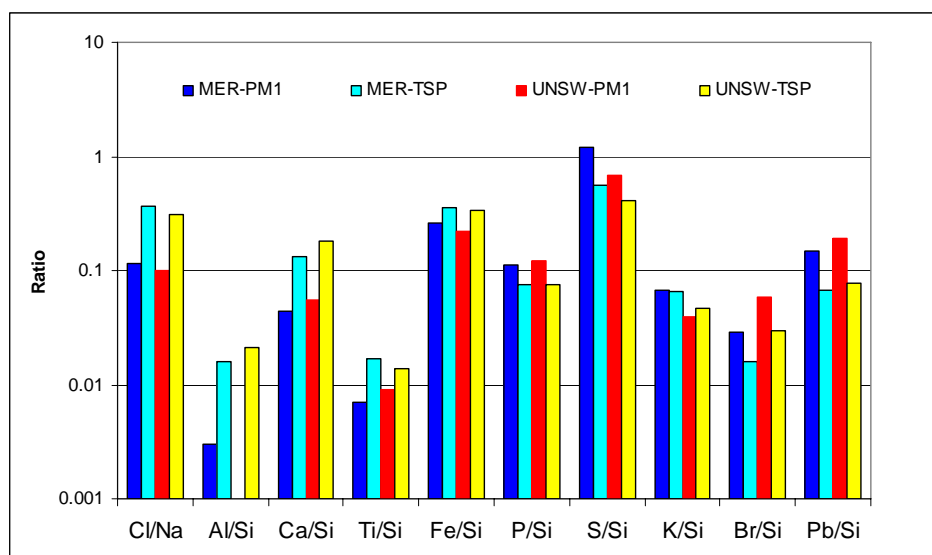


Figure 2. Averages of selected elemental ratios for PM1 and TSP for both Merrylands and UNSW.

3.2 Size-resolved Chemical Composition

The chemical composition generally varies with size, reflecting the different source contributions to aerosols in the atmosphere. To illustrate this, we have plotted the mass concentrations for each stage, along with Na and Cl on the same graph (Figure 1).

The differences in mass concentrations between the sites is evident. The mass concentrations at Merrylands was higher than UNSW on all stages. There is also more variation across the stages at Merrylands than at UNSW. It is also noticeable that Na is measured on almost all stages, with higher concentrations on stages 1 – 5.6 μ m however Cl concentrations appear mostly on stages 1 – 5.6 μ m which would be consistent with sea salt.

3.3 Elemental Ratios

Since Si and Na appear on all stages for all samples, ratios of each element against Si, and element against Na were calculated from the PIXE results. These elemental ratios were calculated for each stage then averaged over the stages contributing to PM1 and all stages to determine PM1 and TSP averages. This allowed comparison of differences in the chemical composition between PM1 and TSP, and also between sites. The ratios for selected elements are plotted in Figure 2.

The average ratios compared to Si are generally considerably less than 1, with the exception of S. Other elements which have relatively high ratios are Fe and Ca. In most cases the ratios for Merrylands and UNSW are

quite similar, except for S/Si where the PM1 ratio is nearly double that for UNSW.

The ratio Cl/Na is much less than expected ratio of 1.796 for seawater, suggesting that other Na compounds are also present. The ratio PM1 is only one third of that for TSP indicating that most of the Cl occurs in the larger size fraction as was illustrated in Figure 1

The elements Si, Al, Ca, Ti and Fe are commonly associated with soil and the ratios of these elements with Si can be compared with crustal ratios to gain some insights. The Al/Si ratio is very low compared to the expected crustal ratio of 0.292 and mainly occurs in TSP. The Ca/Si and Ti/Si ratios are comparable to the crustal ratios for TSP while for PM1 they are about half. The dominance of Ca and Ti in the TSP fraction is consistent with these being from soil or dust. The Fe/Si ratio is higher than the crustal value for both PM1 and TSP. The PM1 value is only slightly higher but the TSP value is around double suggests another source or sources besides soil.

In contrast to the elemental ratios discussed above, for the ratios P/Si, S/Si, Br/Si and Pb/Si, the PM1 ratio is larger than the TSP ratio, and in many cases it is almost double. The K/Si ratio is much the same for PM1 and TSP for both Merrylands and UNSW, with the Merrylands values being close to the crustal value and the UNSW values about half the crustal value.

4. DISCUSSION AND FURTHER WORK

The preliminary results presented here show that there are variations in mass concentrations between Merrylands and UNSW, with the average aerosol loading at Merrylands

being higher than that at UNSW. For both sites the PM1 size fraction accounts for about half of the total mass and the average ratios PM1/TSP, PM1/PM2.5 and PM2.5/TSP are quite similar for both sites.

Differences in size-resolved chemistry have been identified. As would be expected elements associated with sea salt and soil are more abundant in the coarser size fractions.

More detailed analysis of these measurements is planned, including investigation of the influence of meteorological conditions. Further sampling will also be done in order to get complete seasonal coverage. When analysis of the chemical composition is completed, we plan to use the chemical composition to calculate the refractive index for Sydney.

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