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APPORTIONMENT OF SOURCES OF FINE AND COARSE PARTICLES IN FOUR MAJOR AUSTRALIAN CITIES BY POSITIVE MATRIX FACTORISATION

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Abstract

In this study 437 days of 6-daily, 24-hour samples of PM$_{2.5}$, PM$_{2.5-10}$ and PM$_{10}$ were collected over a 12-month period during 2003-2004 in Melbourne, Sydney, Brisbane and Adelaide. The elemental, ionic and polycyclic aromatic hydrocarbon composition of the particles were determined. Source apportionment was carried out by using the Positive Matrix Factorisation software (PMF2). Eight factors were identified for the fine particle samples including ‘motor vehicles’, ‘industry’, ‘other combustion sources’, ‘ammonium sulphates’, ‘nitrates’, ‘marine aerosols’, ‘chloride depleted marine aerosols’ and ‘crustal/soil dust’. On average combustion sources, secondary nitrates/sulphates and natural origin dust contributed about 46%, 25% and 26% of the mass of the fine particle samples, respectively. ‘Crustal/soil dust’, ‘marine aerosols’, ‘nitrates’ and ‘road side dust’ were the 4 factors identified for the coarse particle samples. On average natural origin dust contributed about 76% of the mass of the coarse particle samples. The contributions of the sources to the sample mass basically reflect the emission source characteristics of the sites. Secondary sulphates and nitrates were found to spread out evenly within each city. The average contribution of secondary nitrates to fine particles was found to be rather uniform in different seasons, rather than higher in winter as found in other studies. This could be due to the low humidity conditions in winter in most of the Australian cities which made the partitioning of the particle phase less favourable in the NH$_4$NO$_3$ equilibrium system. A linear relationship was found between the average contribution of marine aerosols and the distance of the site from the bay side. Wind erosion was found associated with higher contribution of crustal dust on average and episodes of elevated concentration of coarse particles in spring and summer.

Keywords: PM$_{2.5}$, PM$_{2.5-10}$, source apportionment, positive matrix factorisation, PIXE, PAH
1. Introduction

Due to the geological and climatic characteristics of the Australian continent, most of the population in Australia are confined to a small number of coastal cities including the four cities in this study: Melbourne, Sydney, Brisbane and Adelaide (Table 1). The increasing emission of air pollutants as a result of the rapid growth in population and economy in these cities, together with the urban sprawl problem, has raised the concern of the impact of these emissions. Among the problems elevated concentration of airborne particles, in particular the PM$_{10}$ (particles with aerodynamic diameter less than 10 $\mu$m) and PM$_{2.5}$ (fine particles; less than 2.5 $\mu$m), has been associated with adverse health and environmental effects. Therefore information on the sources of emission of these particles is needed for the development of effective control strategies for these particles.

Urban aerosol studies in Australia and overseas have identified a wide range of sources of emission of these particles including natural sources, human activities and also the secondary formation processes (e.g. Chow et al. 1996, Cohen et al. 2004). The extent of contribution of these sources to the ambient level of particles, however, depends on the size fraction of the particles and the type and extent of human activities in the cities. The Particle Composition in Four Major Australian Cities project funded by the Department of the Environment and Heritage’s Living Cities Program, was aimed to provide information on the composition and sources of airborne particles in the four cities. The project collected PM$_{2.5}$, PM$_{2.5-10}$ (coarse particles; size between 2.5 and 10 $\mu$m) and PM$_{10}$ samples from an urban site and a suburban site in the four cities during March 2003 – May 2004. The elemental and ionic composition of the PM$_{2.5}$ and PM$_{2.5-10}$ samples and the polycyclic aromatic hydrocarbon (PAH) composition of the PM$_{10}$ samples were determined.

Various receptor modelling techniques including the chemical mass balance method, principal component analysis, multiple linear regression and individual particle analysis (e.g. reviewed in Hopke 1985) have been used for source apportionment of urban aerosols. Recently another factor analysis technique, positive matrix factorisation (PMF), has also been used for this purpose (e.g. Juntto and Paatero 1994, Lee et al. 1999). This technique takes into consideration the errors in the data and produces non-negative factor loadings and scores.
With careful selection of modelling parameters PMF has been found to be more powerful in source identification than the other factor analysis techniques (e.g. Huang et al. 1999, Hien et al. 2004). This paper discusses the results of application of PMF analysis to the aerosol samples from this project.

2. **Sampling and chemical analysis**

The climate of the four cities reflects their eastern coastal location and position within the subtropical to temperate zone of the Southern Hemisphere (Table 1). In general, the warmer half of the year (November to April) is associated with strong winds, high humidity and heavy rainfall conditions (except for Adelaide which has more rainfall in winter) which could reduce the level of ambient pollutants. The prevailing sea breeze (in the afternoon during winter and for most of the day in summer) brings in sea salt and can inhibit the dispersion of air pollutants out of the cities. In contrast, the cooler half of the year (May to October) is associated with low wind speeds and low precipitation conditions, which could increase the air pollution potential. Crustal matter from inland Australia can be transported into the cities by the westerly wind during the night to morning period.

The westerly prevailing wind persists for most of the day from May to August and the cold fronts in the early spring also bring in inland dust to the cities. Low altitude temperature inversions also occur frequently in winter, increasing the pollution levels in the cities. Increased wind erosion during spring and early summer (September to December) in Brisbane and Sydney, and in summer (December to April) in Melbourne and Adelaide, may also result in dust storms and episodes of elevated concentration of particulate matter in the cities (McTainsh and Boughton 1993).

6-daily, 24-hour (from midnight to midnight) PM$_{2.5}$ and PM$_{2.5-10}$ samples were collected concurrently on Nuclepore filters using dichotomous samplers during 2003. Nuclepore filters were chosen due to its lower detection limit for Proton Induced X-ray Emission (PIXE), Proton Induced Gamma Emission (PIGE) and Integrating Plate Laser Absorption techniques comparing with other filter material such as Teflon (Hawas et al. 2003). It has also been reported in the literature that Nuclepore filters are lower in the loss of nitrate and ammonium ions comparing with that in other filter material such as Teflon (e.g. Modey and Eatough 2003, Kyotani and Iwatsuki 2002). However, in 2004 Teflon filters were used instead of Nuclepore filters. This is because the hydrophilic Nuclepore filters were often clogged up in humid conditions (e.g. cold mornings) and
resulted in the loss of samples. The flow rate of the samplers was 16.7 L min$^{-1}$. In total 437 days of particle
samples were analysed (Table 1). The elemental composition of the dichotomous samples was determined at
ANSTO, while the ionic composition was determined at Griffith University. Concurrent PM$_{10}$ samples were
also collected from the sites on glass fibre filters using high volume samplers. The flow rate of the samplers
was 70 m$^3$ hr$^{-1}$. The PAH composition of the PM$_{10}$ samples were determined by Queensland Health Scientific
Services. Analysis for PAHs involved extraction with a dichloromethane/acetone solvent mixture by
ultrasonication followed by gas chromatography – mass spectrometric (GC-MS) determination. The
methodology was based on USEPA standard methods. The details of these analyses, accuracy and precision of
measurement were presented elsewhere (e.g. Hawas et al. 2003).

Since the errors of PIXE/PIGE analysis were lower for the Nuclepore filters than for the Teflon filters, the PMF
analysis was preformed separately for the samples collected from different cities and on different filter
material. Up to 18 inorganic species were included in the PMF analysis, namely the black carbon (BC), Al, Si,
S, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn and Pb elements, and the soluble Na$^+$, NH$_4^+$, Mg$^{2+}$, Cl$^-$ and NO$_3^-$ ions. On
average, these 18 species accounted for about 41% and 44% of the mass of fine particle samples and coarse
particle samples, respectively. Since only the chemical species with measured concentrations above the
detection limit for the species in more than 30% of the samples in the datasets were included in the analysis
(e.g. Ogulei et al. 2005), the species Al, Ti, Mn, Ni, Cu, Pb and/or soluble NH$_4^+$ were excluded from the
analysis of some of the data sets. The actual number of species included varied from city to city and ranged
from 15 to 18 for the samples collected on Nuclepore filters, and from 12 to 15 for the samples collected on
Teflon filters.

The inclusion of PAH composition and/or information on speciation of organics in source apportionment has
been reported as an effective means of distinguishing emissions from different combustion sources (e.g. Park
and Kim 2005). Although 17 PAHs were included in the PAH analysis only 5 of them were detectable in more
than 30% of the PM$_{10}$ samples, namely benzo(b+k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-
c,d)pyrene and benzo(g,h,i)perylene. These are the relatively involatile PAHs. It has been reported in other
studies that these involatile PAHs are associated with the fine particle fraction as a result of rapid adsorption of
PAHs on pre-existing particles, while the more volatile PAHs are more associated with the coarse particle fraction as a result of condensation of PAH vapour (e.g. Harrison et al. 1996, Allan et al. 1996). Therefore in this study these 5 PAHs were assumed to exist mainly in the fine particle fraction and were included in the PMF analysis of the fine particle samples.

The average composition of the samples and percentage of samples above the minimum detection limit (MDL) for the species are listed in Table 2. When calculating the average concentrations the concentration values below MDL were assumed as 0.5 MDL. But in the source apportionment these values are treated as missing values (refer to Section 3.2). Also ng/m$^3$ rather than µg/m$^3$ were used as the unit for concentration due to the low concentrations of the PAHs. Finally those samples which have more than half of the species with measured concentrations below detection limits were also excluded from the PMF analysis. In total 417 days of fine particle samples and 432 days of coarse particle samples were analysed.

3. Source apportionment by PMF

3.1 PMF principles

The 2-dimensional positive matrix factorisation model (PMF2) for source apportionment of urban aerosol samples is (Paatero 2004)

$$X = GF + E \quad [1]$$

where $X(n \times m)$ is the measured composition matrix, $n$ and $m$ are the number of samples and species, respectively. $G(n \times p)$ is the contribution matrix where $p$ is the number of source factors extracted. $F(p \times m)$ is the factor score matrix. $E(n \times m)$ is the unexplained part of $X$. The elements in $G$ and $F$ are constrained to non-negative values only. The objective of PMF analysis is to minimise the value of $Q$, which is defined as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{e_{ij}}{s_{ij}} \right)^2 \quad [2]$$
where $e_{ij}$’s are the elements in $E$ and $s_{ij}$’s are the estimated standard deviations (s.d.) of the measured concentrations.

3.2 Choice of modelling parameters and number of factors

Careful selection of modelling parameters and the number of factors is essential in getting sensible results from PMF analysis. This selection process is still largely by trial-and-error and the experience reported by other researchers (Paatero 2004).

Treatment of concentrations below MDL: In this study two treatments were experimented: assuming these concentrations and their s.d. both as 0.5 MDL (e.g. Song et al. 2006); and treating these values as missing values and assuming the s.d. as 10 times the normal error values (e.g. Paatero 2004). The former treatment was found to result in erroneous source profiles. The latter treatment resulted in source profiles that could be related to physical sources and therefore was used in this study.

Estimation of standard deviations: The s.d. of the species measured by PIXE/PIGE were basically estimated from the MDL and errors in the PIXE/PIGE analysis:

$$s.d. = MDL + \text{Average error to concentration ratio} \times \text{Concentration} \quad [3]$$

The s.d. of the species measured by ion chromatography were estimated by multiplying the concentrations by the Coefficients of Variation (CV) of the species, which are the ratios of s.d. to concentration in the replicate analyses of selected samples. For the PAHs since the chemical analysis used up all the available sample filter area, replicate analysis could not be carried out. RSD% values ranging from <8% (e.g. Crimmins and Baker 2006), to 10% (Environment Australia 2003) and >20% (Fraser et al. 2002) have been reported for PAH analysis using GC-MS techniques in the literature, depending on factors such as sampling time and area of filter analysed. As such the CV of the PAHs was assumed as 0.1 in this study based on the sampling time and filter area analysed comparing with those in the other studies. For the determination of BC a uniform specific

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absorption coefficient, $b_{ap}$ of 7 m$^2$g$^{-1}$ has been used in the project (based on Cohen et al. 2000). But the actual coefficient is dependent on particle size, composition as well as the possible effect of layering of particles on the filters and so may vary by up to a factor of two (Environment Australia 1999). In this study it was found that assigning a larger CV% value of 30% for BC resulted in better values of statistical indicators including $Q$ and explained variations of the species (EV). A 5% sampling error was also assumed for the measured concentrations of the coarse particle samples to account for sources of error such as the bouncing off of coarse particles from the filters during sampling.

Rotational freedom parameter, $F_{\text{peak}}$: The $F_{\text{peak}}$ parameter controls if extreme values are to be assumed for the source matrix $F$ (by assigning positive $F_{\text{peak}}$ values) or the contribution matrix $G$ (negative $F_{\text{peak}}$ values).

Other parameters: In this analysis 10 random starts were computed for each city/filter run to ensure no local minima of $Q$ values were observed. The use of Robust mode together with the value of 4 times the s.d. of the species to define outliers, was also used to minimise the distortion of data set by the outliers.

Selection of number of factors: For each run PMF2 generates a scaled residual matrix ($R$) in which

$$r_{ij} = e_{ij} / s_{ij} \quad [4]$$

The appropriate number of factors extracted for each city was then determined based on the satisfying of most of the following criteria (the first three criteria were based on Lee et al. 1999):

- Value of $Q$ close to nm-pm-pn (i.e. the degree of freedom of the analysis).
- $R_{90}$ (the 90 percentile of the scaled residuals, $r_{ij}$’s) is within ±2. That is, most of the residuals are within 2.
- A sharp drop in IM (the maximum of the mean values of $r_{ij}$’s of each species) and/or IS (the maximum of the s.d. of $r_{ij}$’s of each species).
- Reasonable Cl$^-$ / Na$^+$ ratio (between 1 and 2) in the ‘marine aerosols’ factor (Goldberg 1963).
• Reasonable $\text{NH}_4^+/\text{S}$ ratio (around 1; assuming (NH$_4$)$_2\text{SO}_4$ as the main form of secondary sulphates) in the ‘ammonium sulphates’ factor.

• Reasonable estimated source profiles (refer to Section 3.3). For example, the sum of the fraction of elements should be $\leq 1$.

3.3 Development of source profiles and estimation of source contributions

If all the chemical species of the particles have been analysed and included in the PMF analysis (which can rarely be done in aerosol studies), then the G-factor scores would represent the actual contribution of the sources to the aerosol mass. The 18 main species included in the PMF analysis in this study, however, contributed on average only 41-44% of the aerosol mass. The rest of sample mass was due to undetermined elements such as the organic carbon, hydrogen and oxygen. In this study, a procedure described in Hopke (1989) and used in various source apportionment studies (e.g. Hien et al. 2004, Ogulei et al. 2005), was used to estimate the source contributions to the aerosol mass. After the appropriate number of factors has been determined, the aerosol mass of the samples was used to calculate the scaling factors for each source factor in the G matrix by multiple linear regression between the aerosol mass and the G-factor scores.

\[ M = GA + E' \]  

Where $M(n \times 1)$ is the aerosol mass matrix. The elements in $A(p \times 1)$ are the scaling factors for each source factor. $E'(n \times 1)$ is the error matrix to be minimised. The scaled G-factor scores then represent the source contributions, while the F-factor loadings scaled by the reciprocal of the elements in $A$ represent the source profiles. Since the 18 species included in the PMF analysis were unlikely to contribute to most of the aerosol mass, a small number of samples which have total concentration of the measured species more than 80% of the measured aerosol mass were also excluded from the regression. Negative scaling factors, and/or sum of the fractions of species much greater than one in the scaled source profiles, indicates excessive number of factors has been included in the PMF analysis (e.g. Ogulei et al. 2005).

4. Results and discussions
4.1. Identified sources and source profiles

Up to eight source factors (fine fraction) and four source factors (coarse fraction) were identified in the PMF analysis, respectively. The overall average composition of these factors obtained from the 8 city/filter datasets (4 cities × 2 filter types) are shown in Figure 1 (fine fraction) and Figure 2 (coarse fraction), respectively. While these factors explained >75% of the variations in most species, >30% of the variations in BC, Ni, Cu, Zn, Pb and the PAHs were not explained by these factors. These species have large uncertainty in the measurement method and/or large number of samples which have concentrations below detection limit (Table 2).

More factors were identified in the Melbourne samples, mainly because smaller 37 mm diameter filters were used at the Melbourne sites, which resulted in a higher particle density on the filter and thus lower detection limits in PIXE/PIGE analysis. The average composition of the source factors obtained from samples collected on Nuclepore filters are comparable to those from samples collected on Teflon filters. For example, the average source profiles of coarse particles for the two filter material are shown separately in Table 3. As shown in Table 3, the source profiles were similar for the two filter material, in particular for the tracer species. The PMF2 software also provides estimation on the uncertainty of the F-factor loadings. In the fine particle samples the uncertainty of the loadings (represented by the ratio of the s.d. of loading to the estimate of loading) ranged mostly from ±39% to ±172%. In the coarse particle samples the uncertainty of the loadings ranged mostly from ±20% to ±141%. In general the uncertainty in the estimated factor loadings were lower for the coarse particle samples and for the samples collected on Nuclepore filters.

The ‘crustal/soil dust’ factor has an Al/Si ratio of 0.34. This ratio is similar to that in a dust fall sample collected during a major dust storm event in 1965 in Brisbane (Al/Si = 0.41; Chan et al. 1999). The lower Si % (7%) and higher BC % (14%) in the factor, comparing with those in the above-mentioned dust storm sample (Si 18%, BC 8%) also indicate mixing with emissions from combustion sources.

The ‘marine aerosols’ factor and the ‘chloride depleted marine aerosols’ factor were both identified in the PMF analysis of the fine particle samples. The lower Cl/Na\(^+\) ratio of 1.3 in the ‘marine aerosols’ factor comparing to
that in surface sea water of 1.8 (Goldberg 1963) indicates partial evaporation of the chlorine element. The composition of the ‘chloride depleted marine aerosols’ factor indicates replacement of chloride by sulphate. One or both of these two marine aerosol factors have also been identified in various studies. For examples, similar to our study Kim and Hopke (2004) and Lee et al. (1999) also identified both factors and found similar level of factor contributions to the aerosol mass. Ogulei et al. (2005) identified the ‘chloride depleted marine aerosols’ (‘aged sea salt’) factor but not the ‘marine aerosols’ factor, while in some other studies only the ‘marine aerosols’ (‘sea salt’) factor was identified (Li et al. 2004, Wang and Shooter 2005, Pere-Trepat et al. 2007, Rizzo and Scheff 2007). Also in a Hanoi study the ‘chloride depleted marine aerosols’ factor was only associated with samples of which the wind trajectories were originated from inland (Hien et al. 2004). In our study no significant correlation was found between the contribution of the ‘chloride depleted marine aerosols’ factor and the prevailing wind direction. Instead the average contribution of this factor was found to correlate to the reciprocal of the distance of the site to the bay side ($R^2=0.73$). This indicates that the ‘chloride depleted marine aerosols’ in this study are probably the aged sea salt which gradually changed in composition and particle size over time, and existed as part of the background dust at the coastal sites.

The ratio of $\text{NH}_4^+/\text{S}$ of 1.49 in the ‘ammonium sulphates’ factor indicates the secondary sulphates exist mostly in the completely neutralised form ($\text{NH}_4\text{H}_2\text{SO}_4$. The ‘nitrates’ factor is enriched with Na, $\text{NO}_3^-$, BC and PAHs followed by $\text{NH}_4^+$, indicating $\text{NaNO}_3$ followed by $\text{NH}_4\text{NO}_3$ as the main chemical forms and an incomplete combustion origin.

The ‘motor vehicles’ factor is enriched with BC, heavy metals (Fe, Cu and Zn), $\text{NO}_3^-$ and PAHs. The ‘other combustion sources’ factor is enriched with a similar group of elements as the ‘motor vehicles’ factor. Actually it was found that if the PAHs are not included in the PMF analysis, the ‘other combustion sources’ factor cannot resolved from the ‘motor vehicle’ factor. Comparing with the ‘motor vehicles’ factor, the ‘other combustion sources’ factor is lower in BC and benzo(g,h,i)perylene but higher in K, Cl, K/Al ratio and Cl/Na ratio. Based on the source profiles of emissions from motor vehicle and biomass burnings reported in the literature (e.g. Khalil and Rasmussen 2003, Zou et al. 2003, Bourotte et al. 2005, Park and Kim 2005), this comparison indicates that the ‘other combustion sources’ factor could partly be related to biomass burning
sources including domestic wood heaters, controlled burnings and bush fires. The ‘industry’ factor is enriched with BC, heavy metals and S.

4.2 Contribution of sources to fine and coarse aerosol mass

The average aerosol mass of the samples are shown in Table 4. In general the sample mass was higher at the urban sites than the suburban sites on average. On average the fine particle fraction contributed to about 38% of the PM$_{10}$ mass, which is at the lower end of the range of average PM$_{2.5}$/PM$_{10}$ ratios observed in other urban areas (e.g. 35% in Sao Paulo, Brazil (Bourotte et al. 2005), 37-44% at urban and kerbside locations in European cities (Querol et al. 2004), 45% in Auckland, New Zealand (Wang and Shooter 2005), and 60% in Beijing, China (Song et al. 2006)). The average PM$_{2.5}$/PM$_{10}$ ratios were also rather similar between the urban samples and the suburban samples for each city, with Adelaide samples having a lower PM$_{2.5}$/PM$_{10}$ ratio (Table 4). The lower PM$_{2.5}$/PM$_{10}$ ratio observed in this study indicates a relatively lower contribution of human activities to PM$_{10}$ mass in the 4 Australian cities.

The average contribution of the source factors to the aerosol mass of the site samples are shown in Figure 3 (fine fraction) and Figure 4 (coarse fraction), respectively. PMF software also provides estimation on the uncertainty of the estimated G-scores (source contributions). Similar to the factor loadings, in general the uncertainty in the estimated factor scores was also lower for the Nuclepore filters and for the coarse particle samples. For example, in the Melbourne samples the uncertainty of the scores ranged from ±11% (for ‘marine aerosols’ contribution in the coarse particle samples collected on Nuclepore filters) to ±75% (for ‘industry’ contribution to fine particle sample mass collected on Teflon filters).

The eight factors identified for the fine particle samples included ‘motor vehicles’ (contributing to 24% of the sample mass on average), ‘industry’ (14%), ‘other combustion sources’ (8%), ‘ammonium sulphates’ (18%), ‘nitrates’ (7%), ‘marine aerosols’ (12%), ‘chloride depleted marine aerosols’ (8%) and ‘crustal/soil dust’ (6%). Therefore on average combustion sources, secondary nitrates/sulphates and natural origin dust contributed about 46%, 25% and 26% of the mass of the fine particle samples, respectively. ‘Crustal/soil dust’ (38% of the sample mass on average), ‘marine aerosols’ (38%), ‘nitrates’ (19%) and ‘road side dust’ (5%) were the factors
identified for the coarse particle samples. Therefore on average natural origin dust contributed about 76% of the mass of the coarse particle samples.

The contribution of the source factors to the sample mass of the city/site samples basically reflect the emission source characteristics of the sites (Table 1) and the composition of the samples (Table 2). For examples, as shown in Figure 3 the Sydney site samples have more contribution of ‘ammonium sulphates’ comparing with those from the other cities, reflecting the higher energy use in Sydney and therefore higher emissions from coal-fired power stations. As shown in Figure 3 and Figure 4 the contributions of ‘vehicular dust’ and ‘road side dust’ were higher at the urban sites than at the suburban sites. The contribution of the ‘other combustion sources’ factor, which is partly related to biomass burning activities including domestic wood heaters, controlled burnings and bush fires, was higher at the suburban sites in general. The contribution of the ‘industry’ factor was in general only slightly higher at the suburban sites, probably because of more industrial activities in the suburbia and the effective dispersion of industry dust from stacks. On the other hand, the contributions of ‘ammonium sulphates’ and ‘nitrates’ were similar at the urban sites and the suburban sites, indicating that these secondary aerosols are spread out evenly in the cities. The contributions of secondary sulphates and nitrates were probably underestimated due to loss of NH₄⁺ and NO₃⁻ ions from the filter material.

The combined average percentage contributions of the primary, human activities related sources to the average PM₁₀ mass (excluding crustal/soil dust, marine aerosols, sulphates and nitrates) at the two sites in each city are also compared with the percentages of emission of similar sources in the 2003/2004 PM₁₀ emission inventories of the city (NEPC 2007) in Table 5. Bear in mind that only two sites in each city were included in this study, the results of % source contributions from this study are roughly comparable to the % source emissions.

The contribution of the ‘crustal/soil dust’ factor was similar at the urban sites and the suburban sites, except for the Rocklea site (Brisbane) which has a higher contribution of crustal matter. This is probably due to that the Rocklea site is located in a former paddock area. The Adelaide samples on average were higher in contribution from crustal matter, reflecting the impact of more frequent windblown dust events in the southern part of Australia (McTainsh and Boughton 1993).
The average contribution of ‘marine aerosols’ and/or ‘chloride depleted marine aerosols’ was found to relate to the proximity of the sites to the bay side. For the fine particle fraction, the average contribution of marine aerosols (y; in ng/m$^3$) was related to the reciprocal of the distance of the site from the bay side (x; in m$^{-1}$) by, $y = 2800 \times x + 900$ ($R^2=0.46$; Figure 5). And for the coarse particle fraction, $y = 16000 \times x + 2000$ ($R^2=0.88$). These relationships could be used for rough estimation of long term average contribution of marine aerosols to the particle mass at coastal sites in Australia.

A comparison of the results of source apportionment of fine and coarse particles compiled from this study and other recent aerosol studies is shown in Table 6. This comparison has to use caution because of the samples being taken in different urban locations and from different time periods. There are substantial variations in the number, types and contribution of source factors resolved from the studies. In general, the average aerosol mass and source contributions of the 4 Australian cities were similar to those of Auckland (New Zealand) and lower than those of other cities. The marine aerosols factor was not identified in some non-coastal cities (e.g. Beijing). The contribution from combustion sources varied substantially in the cities and was not identified in the coarse particle fraction in this study and the Auckland study.

4.3 Temporal variations in contribution of sources

The average contributions of the source factors to the mass of the samples collected on weekdays and weekend days, and collected in different seasons are shown in Figure 6 (fine fraction) and Figure 7 (coarse fraction), respectively. The average contributions of motor vehicle related sources and other combustion sources were 40-50% higher in the weekday samples comparing with those in the weekend day samples. The contributions of secondary sulphates and nitrates, industry and marine aerosols, however, did not show significant weekday variations.

Higher aerosol mass and source contributions were observed in the 2004 samples comparing with those in the 2003 samples on average for both particle fractions. This trend is also confirmed by the results of ongoing monitoring of PM$_{2.5}$ and PM$_{10}$ at the sites and indicates higher particle pollution in 2004 comparing with 2003
in the cities. For the fine particle samples, the contributions of crustal sources and combustion sources were higher in the cooler seasons than in the warmer seasons. This is probably due to the decrease in efficiency of vehicle engines in cold weather, the increase in domestic wood heating and also the more frequent temperature inversion phenomenon in the cooler seasons. The contributions of marine aerosols, secondary sulphates and industry were higher in the warmer seasons. This is probably due to the stronger sea breeze, the increase in photochemical activity and higher energy demand in the warmer seasons. Similar seasonal trends in contributions from human activities and secondary sulphates have also been reported in other studies (e.g. Liu et al. 2005, Ogulei et al. 2005).

The average contribution of nitrates to fine particles was rather uniform in the different seasons, which is different to the trend observed in other studies (e.g. Liu et al. 2005, Ogulei et al. 2005). In these studies nitrate contribution in the fine fraction was found to be higher in winter, due to the combination of cold and humid conditions which favour the partitioning of the particle phase in the NH$_4$NO$_3$ equilibrium system. The lack of significant seasonal variations in nitrate contribution to fine particles in this study could be due to the lower humidity in winter in the cities in this study (except Adelaide). Also the drought conditions in recent years in Australia have reduced the humidity further in general. The average contribution of nitrates to coarse particles, on the other hand, was found to be higher in summer. This finding is consistent with that in other studies (e.g. Kocak et al. 2004, Utsunomiya and Wakamatsu 1996). Coarse nitrates exist mainly in the form of NaNO$_3$ as a result of the reaction between HNO$_3$ vapour and sea salt, both are higher in concentration under the stronger sunlight and prevailing sea breeze conditions in summer in Australia.

The average contribution of crustal sources in the coarse fraction was higher in spring/summer than in winter in all cities although this trend was less apparent in Brisbane. Time series plot of the contribution of coarse crustal/soil dust in the cities (e.g. Figure 8 for the Sydney samples) shows that the higher contribution was mainly due to the more frequent episodes of elevated contribution. This reflects the increased frequency of wind erosion in spring/summer, in particular in the southern cities (McTainsh and Boughton 1993). It is also found that these episodes did not always accompany with an increase in fine particle mass, indicating that wind erosion dust is mostly in the coarse particle fraction.
Summary

Source apportionment was carried out for 437 days of fine and coarse particle samples collected during 2003-2004 in Melbourne, Sydney, Brisbane and Adelaide by PMF analysis. The uncertainty in the source apportionment estimates was in general lower for the coarse particle samples and for samples collected on Nuclepore filters. The eight factors identified for the fine particle samples included ‘motor vehicles’, ‘industry’, ‘other combustion sources’, ‘ammonium sulphates’, ‘nitrates’, ‘marine aerosols’, ‘chloride depleted marine aerosols’ and ‘crustal/soil dust’. On average combustion sources, secondary nitrates/sulphates and natural origin dust contributed about 46%, 25% and 26% of the mass of the fine particle samples, respectively. ‘Crustal/soil dust’, ‘marine aerosols’, ‘nitrates’ and ‘road side dust’ were the factors identified for the coarse particle samples. On average natural origin dust contributed about 76% of the mass of the coarse particle samples.

The contributions of the sources to the sample mass basically reflect the emission source characteristics of the sites. Similar average contributions of secondary sulphates/nitrates and industry dust were observed at the urban site and the corresponding suburban site in the cities, reflecting the secondary formation nature of the sulphates/nitrates and the effective dispersion of industry dust from stacks. A linear relationship was found between the average contribution of marine aerosols and the distance of the site from the bay side. Wind erosion was found associated with higher crustal dust contribution on average and episodes of elevated coarse particle mass in spring and summer.

The average contribution of combustion sources were 40-50% higher in the weekday samples than in the weekend day samples. The contributions from combustion sources were in general higher in the cooler seasons, while contributions from secondary sulphates were higher in the warmer, humid seasons. The average contribution of secondary nitrates to fine particles was found to be rather uniform in different seasons, rather than higher in winter as found in other studies. This could be due to the lower humidity in winter in most of the cities in this study which reduced the humidity in general and made the partitioning of the particle phase less favourable in the NH₄NO₃ equilibrium system.
The average fine particle to PM$_{10}$ mass ratio in the Australian city samples in this study was at the lower end of the ratios observed in other cities. The results of aerosol mass and source contributions for the Australian cities in this study were similar to those found in Auckland (New Zealand), and were generally lower than those from other cities around the world.

**Acknowledgments**

We would like to acknowledge the help of staff from state EPAs for regular filter changes throughout the study. The project is funded by Department of the Environment and Heritage’s Living Cities Program.

**References**


Environment Australia 1999, *Chemical and physical properties of Australian fine particles: a pilot study.*


Captions

Table 1. Sampling sites and number of samples (in bracket)

Table 2. Average composition of the samples (average ± s.d. in the samples; in ng/m$^3$)

Table 3. Average source profiles of coarse particle samples collected on Nuclepore filters and on Teflon filters (in % g/g dust)

Table 4. Average aerosol mass of the site samples

Table 5. Comparison of average percentages of source contributions to PM$_{10}$ mass with percentages of PM$_{10}$ emissions from similar sources in the cities

Table 6. A comparison of the results from recent source apportionment studies (averages in ng/m$^3$)

Figure 1. Fine particle source profiles

Figure 2. Coarse particle source profiles

Figure 3. Average contributions of source factors in the fine particle samples from the sites

Figure 4. Average contributions of source factors in the coarse particle samples from the sites

Figure 5. Contributions of marine aerosol and proximity of the site from the bay side

Figure 6. Temporal trends of contributions of source factors in the fine particle samples (in ng/m$^3$)

Figure 7. Temporal trends of contributions of source factors in the coarse particle samples (in ng/m$^3$)

Figure 8. Contribution of crustal/soil dust to coarse particle mass in the Sydney samples (in ng/m$^3$) (solid: Earlwood site samples; broken: Richmond site samples)
<table>
<thead>
<tr>
<th>City</th>
<th>Melbourne</th>
<th>Sydney</th>
<th>Brisbane</th>
<th>Adelaide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location and population</td>
<td>37°47’S</td>
<td>34°0’S</td>
<td>27°29’S</td>
<td>34°55’S</td>
</tr>
<tr>
<td></td>
<td>144°58’E</td>
<td>151°0’E</td>
<td>158°8’E</td>
<td>138°36’E</td>
</tr>
<tr>
<td></td>
<td>3.5 million</td>
<td>4.2 million</td>
<td>1.7 million</td>
<td>1.1 million</td>
</tr>
<tr>
<td>Sampler and filter</td>
<td>Anderson 241 with 37 mm diameter filters</td>
<td>Partisol 2025 with 47 mm diameter filters</td>
<td>Partisol 2025 with 47 mm diameter filters</td>
<td>Partisol 2025 with 47 mm diameter filters</td>
</tr>
<tr>
<td>Urban site</td>
<td>Alphington (65) Residential / light industrial area Site next to a railway station; ~10 km from the bay side</td>
<td>Earlwood (47) Residential area Site ~5 km from the bay side</td>
<td>Rocklea (55) Residential / light industrial area Site ~750 m from a minor road and ~1 km from a major road; former grazing paddock within an animal research farm; ~20 km from the bay side</td>
<td>Netley (38) City / commercial area Site ~500 m from a main road, and ~ 2 km from an aluminium foundry adjacent to airport; ~5 km from the bay side</td>
</tr>
<tr>
<td>Suburban site</td>
<td>Footscray/Paisley 1 (72) Residential / light industrial area Paisley site is inside a high school; ~5 km from the bay side</td>
<td>Richmond (59) Residential / semi-rural area Site inside a university campus; ~60 km from the bay side</td>
<td>Springwood (63) Residential area Site ~1 km from a major road; inside a high school; ~15 km from the bay side</td>
<td>Northfield (38) Residential area Site ~200 m from a major road; ~10 km from the bay side</td>
</tr>
<tr>
<td>Total number of samples</td>
<td>137</td>
<td>106</td>
<td>118</td>
<td>76</td>
</tr>
</tbody>
</table>

1 Dichotomous samples were collected from Footscray. High volume samples were collected from Paisley which is approximately 500 m from Footscray.
Table 2. Average composition of the samples (average ± s.d. in the samples; in ng/m³)

<table>
<thead>
<tr>
<th></th>
<th>··PM_{2.5}··</th>
<th></th>
<th>··PM_{2.5-10}··</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% samples &gt;MDL</td>
<td>Urban site samples concentration</td>
<td>% samples &gt;MDL</td>
</tr>
<tr>
<td>Mass</td>
<td>100</td>
<td>6103 ± 3684</td>
<td>5409 ± 2877</td>
</tr>
<tr>
<td>BC</td>
<td>92</td>
<td>1016 ± 972</td>
<td>735 ± 624</td>
</tr>
<tr>
<td>Al</td>
<td>49</td>
<td>33 ± 127</td>
<td>33 ± 90</td>
</tr>
<tr>
<td>Si</td>
<td>62</td>
<td>67 ± 301</td>
<td>67 ± 221</td>
</tr>
<tr>
<td>S</td>
<td>99</td>
<td>297 ± 307</td>
<td>296 ± 281</td>
</tr>
<tr>
<td>K</td>
<td>99</td>
<td>46 ± 44</td>
<td>45 ± 82</td>
</tr>
<tr>
<td>Ca</td>
<td>97</td>
<td>37 ± 51</td>
<td>34 ± 51</td>
</tr>
<tr>
<td>Ti</td>
<td>32</td>
<td>4 ± 8</td>
<td>4 ± 6</td>
</tr>
<tr>
<td>Mn</td>
<td>64</td>
<td>3 ± 4</td>
<td>5 ± 3</td>
</tr>
<tr>
<td>Fe</td>
<td>99</td>
<td>74 ± 91</td>
<td>41 ± 62</td>
</tr>
<tr>
<td>Ni</td>
<td>32</td>
<td>2 ± 1</td>
<td>1 ± 1</td>
</tr>
<tr>
<td>Cu</td>
<td>59</td>
<td>3 ± 2</td>
<td>2 ± 3</td>
</tr>
<tr>
<td>Zn</td>
<td>83</td>
<td>17 ± 21</td>
<td>11 ± 17</td>
</tr>
<tr>
<td>Pb</td>
<td>38</td>
<td>11 ± 10</td>
<td>9 ± 10</td>
</tr>
<tr>
<td>Soluble Na⁺</td>
<td>99</td>
<td>455 ± 349</td>
<td>403 ± 301</td>
</tr>
<tr>
<td>Soluble NH₄⁺</td>
<td>43</td>
<td>195 ± 455</td>
<td>190 ± 369</td>
</tr>
<tr>
<td>Soluble Mg²⁺</td>
<td>52</td>
<td>28 ± 40</td>
<td>27 ± 38</td>
</tr>
<tr>
<td>Soluble Cl⁻</td>
<td>94</td>
<td>267 ± 356</td>
<td>226 ± 318</td>
</tr>
<tr>
<td>Soluble NO₃⁻</td>
<td>59</td>
<td>126 ± 185</td>
<td>106 ± 171</td>
</tr>
<tr>
<td>Benzo(b+k)fluoranthene</td>
<td>54</td>
<td>0.35 ± 0.56</td>
<td>0.20 ± 0.35</td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>39</td>
<td>0.19 ± 0.32</td>
<td>0.11 ± 0.18</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>31</td>
<td>0.18 ± 0.37</td>
<td>0.11 ± 0.18</td>
</tr>
<tr>
<td>Indeno(1,2,3-c,d)pyrene</td>
<td>41</td>
<td>0.20 ± 0.34</td>
<td>0.12 ± 0.16</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>55</td>
<td>0.35 ± 0.53</td>
<td>0.19 ± 0.29</td>
</tr>
</tbody>
</table>

1. The PAH concentrations were determined from the PM₁₀ samples and were assumed to be mainly associated with the fine particle fraction
2. No data
Table 3. Average source profiles of coarse particle samples collected on Nuclepore filters and on Teflon filters (in % g/g dust)

<table>
<thead>
<tr>
<th></th>
<th>Crustal/soil dust</th>
<th>Road side dust</th>
<th>Marine aerosols</th>
<th>Nitrates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nuclepore</td>
<td>Teflon</td>
<td>Nuclepore</td>
<td>Teflon</td>
</tr>
<tr>
<td>BC</td>
<td>3.30</td>
<td>2.39</td>
<td>7.67</td>
<td>14.62</td>
</tr>
<tr>
<td>Al</td>
<td>3.88</td>
<td>2.86</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>Si</td>
<td>13.14</td>
<td>10.92</td>
<td>0.90</td>
<td>0.68</td>
</tr>
<tr>
<td>S</td>
<td>0.11</td>
<td>0.49</td>
<td>0.68</td>
<td>2.91</td>
</tr>
<tr>
<td>K</td>
<td>1.31</td>
<td>1.38</td>
<td>1.04</td>
<td>2.58</td>
</tr>
<tr>
<td>Ca</td>
<td>3.32</td>
<td>2.70</td>
<td>2.41</td>
<td>3.52</td>
</tr>
<tr>
<td>Ti</td>
<td>0.45</td>
<td>0.46</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
<td>0.09</td>
<td>0.04</td>
<td>0.29</td>
</tr>
<tr>
<td>Fe</td>
<td>4.57</td>
<td>4.10</td>
<td>3.85</td>
<td>2.57</td>
</tr>
<tr>
<td>Cu</td>
<td>0.06</td>
<td>0.02</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.11</td>
<td>0.16</td>
<td>0.14</td>
<td>0.54</td>
</tr>
<tr>
<td>Pb</td>
<td>0.04</td>
<td>0.00</td>
<td>0.13</td>
<td>0.00</td>
</tr>
<tr>
<td>Soluble Na⁺</td>
<td>0.26</td>
<td>1.36</td>
<td>18.39</td>
<td>7.31</td>
</tr>
<tr>
<td>Soluble Mg²⁺</td>
<td>0.05</td>
<td>0.09</td>
<td>11.36</td>
<td>8.28</td>
</tr>
<tr>
<td>Soluble Cl⁻</td>
<td>1.04</td>
<td>1.47</td>
<td>1.66</td>
<td>10.16</td>
</tr>
<tr>
<td>Soluble NO₃⁻</td>
<td>0.07</td>
<td>1.18</td>
<td>1.51</td>
<td>2.71</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>31.82</td>
<td>29.67</td>
<td>50.26</td>
<td>56.46</td>
</tr>
</tbody>
</table>

Table 4. Average aerosol mass of the site samples

<table>
<thead>
<tr>
<th>City</th>
<th>Site</th>
<th>Fine aerosol mass (ng/m³)</th>
<th>Coarse aerosol mass (ng/m³)</th>
<th>Fine fraction of aerosol mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melbourne</td>
<td>Suburban (Footscray/Paisley)</td>
<td>6130</td>
<td>10370</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Urban (Alphington)</td>
<td>6630</td>
<td>8840</td>
<td>0.43</td>
</tr>
<tr>
<td>Sydney</td>
<td>Suburban (Richmond)</td>
<td>5430</td>
<td>9040</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>Urban (Earlwood)</td>
<td>7060</td>
<td>11350</td>
<td>0.38</td>
</tr>
<tr>
<td>Brisbane</td>
<td>Suburban (Springwood)</td>
<td>5170</td>
<td>7150</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Urban (Rocklea)</td>
<td>5380</td>
<td>8210</td>
<td>0.40</td>
</tr>
<tr>
<td>Adelaide</td>
<td>Suburban (Northfield)</td>
<td>5200</td>
<td>12770</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>Urban (Netley)</td>
<td>5700</td>
<td>12980</td>
<td>0.31</td>
</tr>
<tr>
<td>All samples</td>
<td>Suburban sites</td>
<td>5550</td>
<td>9530</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>Urban sites</td>
<td>6210</td>
<td>10020</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>All samples</td>
<td>5860</td>
<td>9760</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Table 5. Comparison of average percentages of source contributions to PM$_{10}$ mass with percentages of PM$_{10}$ emissions from similar sources in the cities

<table>
<thead>
<tr>
<th>City</th>
<th>Average % of source contributions</th>
<th>Percentages of sources PM$_{10}$ emissions from similar sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Roadside dust</td>
<td>Vehicular dust</td>
</tr>
<tr>
<td>Melbourne</td>
<td>21</td>
<td>37</td>
</tr>
<tr>
<td>Sydney</td>
<td>nd</td>
<td>64</td>
</tr>
<tr>
<td>Brisbane</td>
<td>28</td>
<td>40</td>
</tr>
<tr>
<td>Adelaide</td>
<td>nd</td>
<td>45</td>
</tr>
</tbody>
</table>

1 Combining the fine and coarse particle results from this study; excluding the crustal/soil dust, marine aerosols, sulphates and nitrates source factors; the ‘road side dust’ factor was not identified in the Sydney and Adelaide samples

2 Compiled from the 2003/2004 emission data from NEPC, 2007; emissions from paved/unpaved road were not reported for Sydney and Brisbane

Table 6. A comparison of the results from recent source apportionment studies (averages in ng/m$^3$)
Figure 1. Fine particle source profiles
Remarks: The mass % values represent the average % by mass of each species in factors related to the same source extracted from the 8 city/filter datasets (4 cities × 2 filter types). The bars above the averages represent the s.d. in the % by mass values of each species in the source factors extracted from the 8 datasets. The mass % values of PAHs are enlarged by 1000 times for easier viewing.
Figure 1 (continued). Fine particle source profiles.
Figure 2. Coarse particle source profiles
Figure 3. Average contributions of source factors in the fine particle samples from the sites. Remarks: The ‘crustal/soil dust’ factor was not identified in the Brisbane samples; the ‘chloride depleted marine aerosols’ factor was not identified in the Adelaide samples.

Figure 4. Average contributions of source factors in the coarse particle samples from the sites. Remarks: The ‘road side dust’ factor was not identified in the Sydney samples and the Adelaide samples.
Figure 5. Contributions of marine aerosol and proximity of the site from the bay side

Figure 6. Temporal trends of contributions of source factors in the fine particle samples (in ng/m³)
Figure 7. Temporal trends of contributions of source factors in the coarse particle samples (in ng/m³)

Figure 8. Contribution of crustal/soil dust to coarse particle mass in the Sydney samples (in ng/m³)
(solid: Earlwood site samples; broken: Richmond site samples)