

Seasonal and Regional Variations in Ambient Fine Particle Concentrations and Sources in New South Wales, Australia: A Seven Year Study.

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ABSTRACT

Non-destructive accelerator based ion beam analysis (IBA) methods have been used to determine over 20 different chemical species present in ambient atmospheric fine particles in and around Sydney, Australia over a 7 year period. These data have then been used to generate elemental source fingerprints and used in Chemical Mass Balance calculations to determine fine particle (PM_{2.5}) source contributions atmospheric pollution.

INTRODUCTION

Ambient atmospheric fine particle concentrations and composition play a major role in the understanding of pollution transport, visibility and climate change. High concentrations of PM_{2.5} and PM₁₀ particles (that is particles with aerodynamics diameters of 2.5 and 10 microns and less) in the atmosphere have been shown to have significant impacts on human health in major urban areas around the world [1]. To better understand the roll of fine particles in these processes, it is important to quantify the anthropogenic and the natural components, the regional and seasonal variations as well as identify possible sources.

The Aerosol Sampling Project (ASP) at the Australian Nuclear Science and Technology Organisation (ANSTO) has been monitoring and characterising PM_{2.5} and PM₁₀ particles in regions around Australia and overseas since mid 1991. We now have a data set of fine particle data (PM_{2.5}) consisting of thousands of filters collected every Sunday and Wednesday at dozens of different sites. Each of these filters has been analysed using non-destructive accelerator based ion beam analysis (IBA) methods to determine over 20 different chemical species present in ambient atmospheric fine particles [2-5].

PARTICLE SAMPLING PROGRAM

Here we report on sampling at three major industrial and urbanised regions of New South Wales, Australia, Mayfield in Newcastle, Mascot in Sydney and Warrawong in Wollongong, see Fig. 1. These three regions include about 5 million people and cover over 175 km of the NSW coastline. Fine particles (PM_{2.5}) have been collected twice weekly (every Sunday and Wednesday) since before January 1992 on 25 mm diameter stretched Teflon filters using a cyclone size selective inlet with a pumping rate of 22 L/min. Each sample was collected for 24 hours from mid-night to mid-night. Here we report on the 7 year sampling period from January 1992 to December 1998 inclusive. During this period over 2,000 filters were collected at these three sites, weighed and analysed using IBA methods. The stretched Teflon filters were only 220 $\mu\text{g}/\text{cm}^2$ thick with PM_{2.5} mass loading typically between 100 and 300 μg , making them ideal thin targets for IBA analysis.

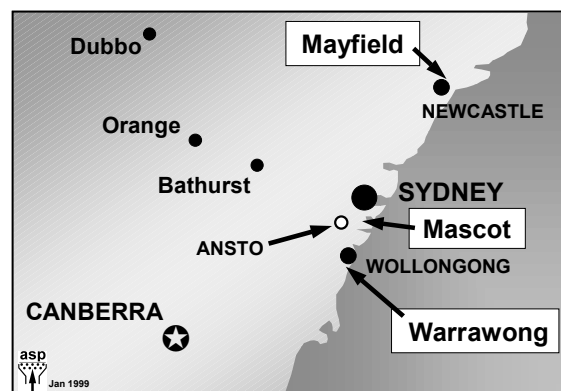


Fig. 1. Location of the Mayfield, Mascot and Warrawong sites on the eastern coast of Australia.

FINE PARTICLE COMPOSITION

Four non-destructive simultaneous IBA methods of PIXE, PIGME, RBS and PESA were used to determine the concentrations of the chemical species H, C, N, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb, soil, ammonium sulphate, organic matter and seaspray. These techniques have been described in detail

elsewhere and will not be further discussed here [2-4] except to say that they have sufficient sensitivity to determine many species to around 1 ng/m³ of air sampled.

Table 1 shows typical concentrations for all the species measured at the Mascot site in central Sydney. The concentrations listed are averages of 24 hour data over the 7 year study period. The errors quoted are standard deviations of the 730 or so samples taken at Mascot. The large errors reflect the seasonal variations in the data not the measurement errors which were typically 5-15%. This is clearly shown in Figs. 2 and 3 where the average monthly data for the total PM2.5 mass and the lead concentrations are plotted as a function of time for the Mascot site. Winter peaks (June to August) in the fine particle concentrations are clearly visible with summer winter variations being more than a factor of four in some years. Similar seasonal variations occur for other elements such as Na, Si, S, Cl, K, Br and Pb.

Species	Conc. [ng/m ³]	Species	Conc. [ng/m ³]
Mass	10,300±4,600	Fe	104±88
H	371±222	Co	0.4±0.4
Na	379±290	Ni	1±1
Al	51±46	Cu	5±3
Si	80±50	Zn	30±24
P	5±3	Br	67±83
S	490±154	Pb	173±175
Cl	462±210	(NH ₄) ₂ SO ₄	2019±640
K	71±40	Soot	3,760±2,470
Ca	50±28	Soil	652±460
Ti	5±3	K _{non}	9±29
V	1±0.5	Organics	2,737±2,300
Cr	1±1	Seasalt	963±740
Mn	10±15		

Table 1. Average concentrations of fine particles at Mascot for the 7 year study period.

In Table 1, fine particle ammonium sulphate was estimated from sulphur and hydrogen assuming full neutralisation; soot was elemental carbon; soil was estimated from the oxides of Al, Si, Ca, Ti and Fe; K_{non} was the non soil potassium and represented smoke and organic matter was estimated from hydrogen assuming an average composition of 9%H, 71%C and 20%O [3-4].

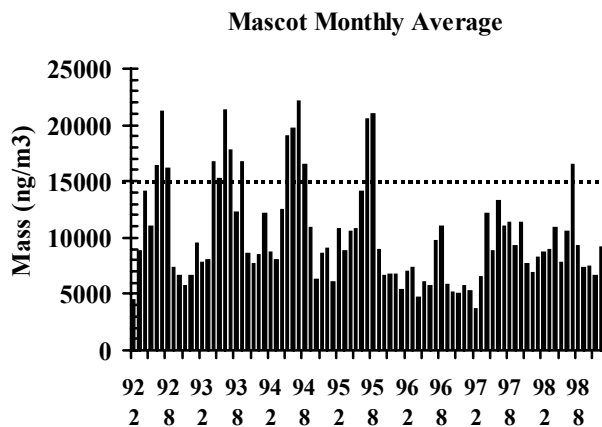


Fig.2. PM2.5 mass with time for January 1992 to December 1998 for the Mascot site in central Sydney. The dashed line is the USEPA annual goal of 15 µg/m³

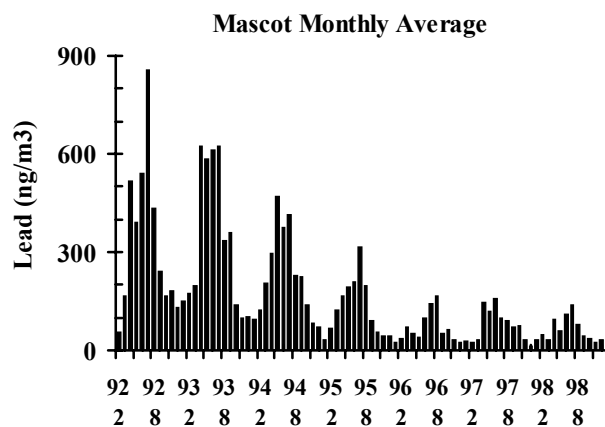


Fig.3. PM2.5 lead with time for period January 1992 to December 1998 for the Mascot site in central Sydney.

Fig. 3 also shows a distinct decrease in the ambient atmospheric fine particle (PM2.5) lead concentrations over the study period. This was due to the reduction of lead in leaded petrol from 0.4g/L in 1993 to 0.3g/L in 1994 and finally to 0.2g/L in 1995 where it currently remains. This had the effect of reducing lead emissions from motor vehicles in Sydney from 1,230 tons per year to 450 tons annually [5].

The fine fraction can be split into 5 major components elemental carbon or soot, organic matter, ammonium sulphate, airborne soil, seaspray and trace elements usually associated industrial activities. In Table 2 we show the relative percentage contributions for each of these major components as well as the PM2.5 total masses at the three study sites averaged over the full 7 year study period. The PM2.5 ambient mass concentrations were below the US EPA (NAAQS) goal of 15 µg/m³ annual average, and generally below the 65 µg/m³ 24 hour goal. The average percentage contributions do not vary much between sites, although the higher elemental carbon and lead at Mascot reflect the higher motor vehicle

contribution at this site and the higher sulphate and soil components at Mayfield and Warrawong reflect the increased industrial activity relative to Mascot site. These inter-elemental associations leading to identification of possible sources can be further tested as many elements have been measured. For example, Pb and Br from the combustion of leaded petrol, K and elemental carbon form biomass burning and Al and Si from airborne soils. The correlation plots of Figs. 4 and 5 show that strong correlations are present for elements associated with particular sources. The gradient of the Pb-Br of Fig. 4 was 2.1, a value of 2.08 was calculated for known bromine/ lead additives in Sydney petrol [5]. The fact that most points lie near or on the least squares fit to the data demonstrates that most of the lead at Mascot is associated with bromine and hence with motor vehicles. Similar plots for the heavy industrial sites of Mayfield and Warrawong show excess lead, above the $[Pb/Br]=2.08$ line, not associated with bromine. Demonstrating other industrial lead sources not associated with motor vehicles. While the gradient of the Al-Si plot of Fig. 5 shows that the average airborne soil at the Lucas Heights site contains about twice as much silicon as aluminium.

PM2.5 7 year Average Species %	Mayfield Newcastle	Mascot Sydney	Warrawong Wollongong
Elemental Carbon	30±11	36±24	25±12
Organics	20±11	27±22	15±8
(NH ₄) ₂ S ₀ ₄	20±6	20±6	27±12
Soil	16±7	6±5	12±5
Sea Salt	9±8	9±7	12±8
Lead	0.6±0.4	1.8±2	0.6±0.4
Trace elements [including NO ₃ , H ₂ O]	<7	<1	<7
PM2.5 Mass (µg/m ³)	12.5±3	10.3±5	9.2±3

Table 2. Percentage contributions of the major components to the PM2.5 mass fraction at the three study sites averaged over the 7 year study period.

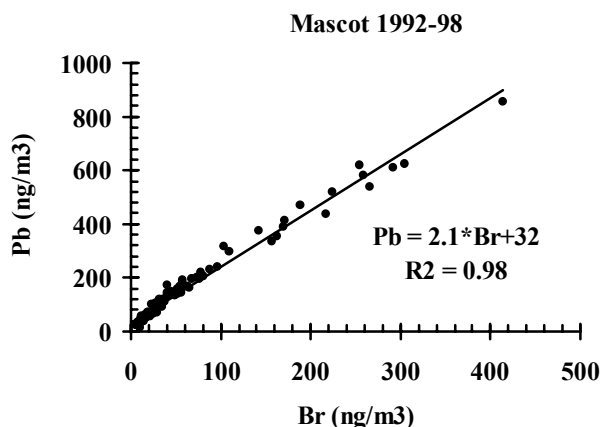


Fig. 4. PM2.5 lead vs bromine at Mascot, demonstrating a major motor vehicle source

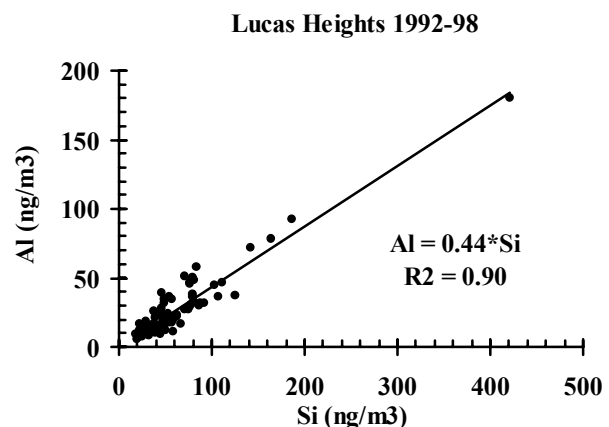


Fig. 5. PM2.5 aluminium vs silicon at the ANSTO site, demonstrating an airborne soil source

PM10 AND PM2.5 VARIATIONS

Since 1994 PM2.5 and PM10 ambient air particulates have also been measured twice a week at two sites in Sydney, one at Liverpool, an urban site, 20 km SW of Sydney and the other at ANSTO (see Fig. 1). These were performed using a stacked filter system with a fine (PM2.5) fraction and a coarse 2.5 to 10 µm fraction obtained on separate Nuclepore filters with the sampling unit operating at 16 L/min [6]. The PM10 fraction was obtained by adding the fine and coarse fractions from the stacked filter unit. Fig. 6 shows the average monthly PM10 and PM2.5 mass fractions for the Liverpool site. The two curves track each other fairly well over several years with the average PM10 mass being (21±7) µg/m³ and the average PM2.5 mass being (7.4±3) µg/m³. Fig. 7 is plot of the PM10 mass fraction against the PM2.5 mass fraction for both sites during 1994-98. It shows the average $[PM10/PM2.5]$ ratio was (2.7±0.8). A plot of the coarse (2.5 to 10 µm) fraction against the PM2.5 fraction showed a poorer correlation than given in Fig. 7 demonstrating that, in Sydney, this ratio is dominated by the fine fraction which is more closely related to possible health effects. A good reason to measure the PM2.5 fraction rather than the PM10 fraction on a regular basis. There was no seasonal variation in the $[PM10/PM2.5]$ ratio over the study period, however there were large variations depending on the nature of the pollution source. For example, when combustion sources like bush fires

dominated the ambient concentration ratios were small, but when dust storms or strong sea breezes dominated the ratios were high, as expected.

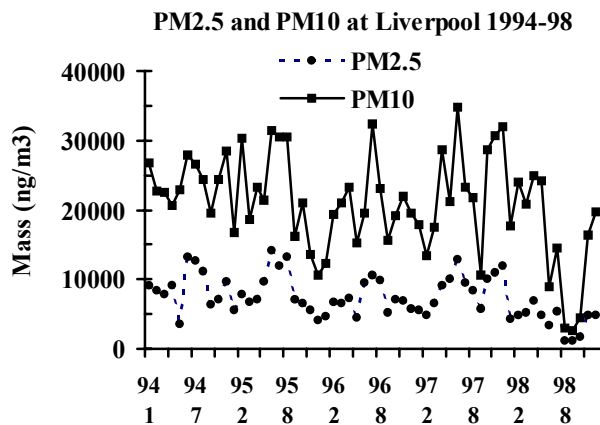


Fig. 6. Average monthly PM10 and PM2.5 mass fractions at Liverpool during 1994-98

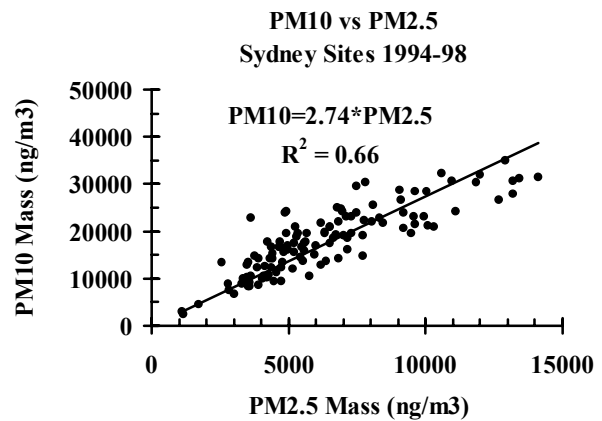


Fig. 7. PM10 versus PM2.5 mass fractions for the Liverpool and ANSTO sites during 1994-98.

SOURCE FINGERPRINTING AND CHEMICAL MASS BALANCE CALCULATIONS

The unique multi-elemental accelerator based ion beam analysis (IBA) methods gave good 'mass closure'. That is the sum of the measured constituents, called the 'reconstructed mass' was close to the measured gravimetric mass. For the three sites considered here the average reconstructed masses were (87±10)%, (91±10)% and (97±11)% at Warrawong, Mayfield and Mascot respectively over the 7 year study period. This is excellent considering that we estimate between 5% and 10% of the gravimetric mass is due to water vapour which is lost as we perform our IBA techniques in vacuum. Furthermore, the multi-elemental nature of the analyses produced more than 20 different chemical species that were combined with the hundreds of filters and standard Principal Component Analysis (PCA) methods to define elemental source fingerprints [2,3,7,8]. Generally the data required between 3 and 6 principal components to explain 70 % to 90% of the sample variance. Each of these principal components or fingerprints was given a generic name that best reflected its elemental source components. The six unique fingerprint names and their associated element as defined by PCA methods are shown in Table 3. These source fingerprints and their relative elemental contributions are unique to the Sydney data set as they were derived statistically entirely from this data set [2,3,4]. Fingerprints for other sites in other countries may contain quite different elements and will certainly contain different elemental ratios within a fingerprint.

Fingerprint	Elements Used
Motor Vehicles	H, Na, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Pb, Elt.C
Soil	Al, Si, K, Ca, Ti, Mn, Fe
Seaspray	Na, S, Cl, K, Ca, Br
Smoke	H, P, Cl, K, Ca, Mn, Elt.C
Coal	H, Na, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Elt.C
Industry	H, P, S, V, Cr, Co, Ni, Cu, Zn, Pb, Elt.C

Table 3. Elements selected by Principal Components Analysis as being associated with selected source fingerprints.

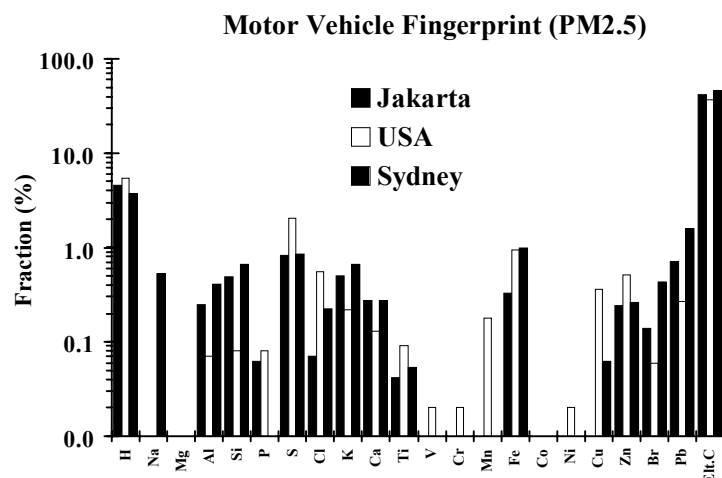


Fig. 8 Motor vehicle fingerprints for PM2.5 particles for Jakarta, Sydney and the USA [4].

By the appropriate examination of data from selected sampling sites the relative contributions of each of these elements to a given fingerprint can be determined [2,3]. For example, in Fig. 8 we show one such fingerprint obtained for motor

vehicles for three different sampling studies performed in Jakarta, Sydney and the US. The elemental composition of the three fingerprints are remarkably similar differing in the lead and bromine additives, as expected, and in some minor trace elements. All fingerprints contained elemental components related to retrained soil (Al, Si, Ti) associated with motor vehicle movements.

Having defined a set of source fingerprints, similar to those in Fig. 8, that span the data set it is possible to include these in a Chemical Mass Balance (CMB) analysis [9] to produce both absolute ($\mu\text{g}/\text{m}^3$) and percentage contributions of these fingerprints to the total mass loadings on the filters. Table 4 show the results from such a CMB calculation for monthly values averaged over the 7 year

study period at the Mayfield, Mascot and Warrawong sites. The values listed are percentage contributions for each source fingerprint to the total PM_{2.5} mass loadings given at the bottom of Table 2. Again the standard deviations given were large as they reflected the seasonal variations in the source contributions not the errors in the CMB statistical fits to the data. The numbers in brackets after the errors are the maximum average monthly values for each source over the

7 year Average Percentage Concentrations	Mayfield Newcastle	Mascot Sydney	Warrawong Wollongong
Motor Vehicles	33 ± 17(73)	52 ± 22(87)	27 ± 11(58)
Seaspray	10 ± 5(24)	11 ± 9(33)	11 ± 7(28)
Soil	13 ± 6(28)	1.7 ± 1.5(6)	11 ± 4(24)
Smoke	1.6 ± 6(26)	0.5 ± 4(27)	2 ± 7(28)
Industry	43 ± 10(62)	35 ± 16(73)	49 ± 11(71)

Table 4. Average percentage source contributions for Newcastle, Sydney and Wollongong sites for the 7 year study period from January 1992 to December 1998.

7 year study period. Fine particle pollution at the inner Sydney city site of Mascot is clearly dominated by motor vehicles, having a maximum monthly average of nearly 90% in the winter months of some years. The seaspray component was consistently around 10% or 11% for all sites as they are coastal sites (see Fig. 1). The airborne soil fingerprint at Mascot was lower than the total soil content at Mascot as given in Table 2 because some of the soil components appeared in the motor vehicle fingerprint as well, as discussed earlier and also shown in Fig. 8. Smoke from biomass burning is associated with domestic wood burning for heating and controlled burning in the winter as well as the occasional bushfire in the summer. This is reflected in the high maximum values, given in brackets, compared with the relatively low average annual contributions.

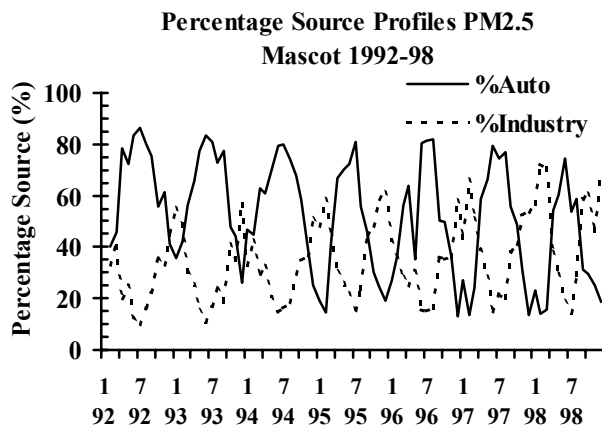


Fig. 9. Percentage source fingerprint contributions for motor vehicles and industry at Mascot for PM_{2.5} particles for 1992-98

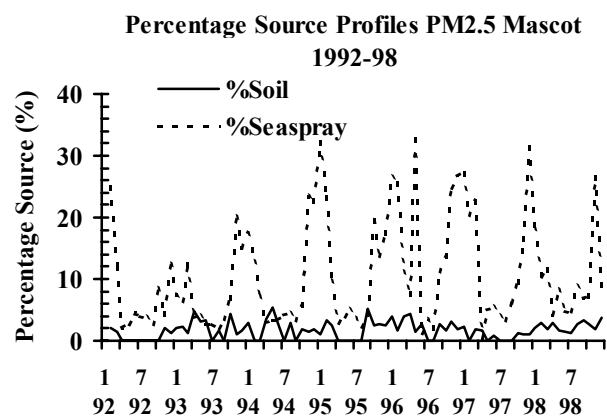


Fig. 10. Percentage source fingerprint contributions for soil and seaspray at Mascot for PM_{2.5} particles for 1992-98

Figs. 9 and 10 show the CMB calculations for the average monthly contributions for the motor vehicle, industry, soil and seaspray fingerprints for Mascot site for the period from January 1992 to December 1998 inclusive. The seasonal variations of the motor vehicles and industry fingerprints are obvious, with the seven winter peaks for motor vehicles and the six summer peaks for the industry fingerprints. The industry fingerprint was dominated by the high fine particle sulphate component which has sunlight as a catalyst for its production. Hence higher industry fingerprints in

the summer. Whereas the motor vehicle highs in the winter were produced by cooler calmer weather conditions and inversion layers. Hence Sydney has a fine particle pollution problem dominated by motor vehicle emissions in the winter and industry emissions in the summer. These summer/ winter variations in the fingerprint contributions can vary by factors of 3 or 4 showing the need to maintain sampling at a given site for at least several annual cycles. Similar plots were obtained for the industrial sites at Mayfield and Warrawong.

CONCLUSION

Through the simultaneous application of four ion beam analysis techniques, namely PIXE, PIGME, RBS and forward recoil analysis, we have been able to fully characterise fine particle filters for a range of elements from hydrogen to lead. Since 1991 we have analysed over 14,000 filters from more than 50 samplers in this way. The collection of such a large dataset has enabled statistical approaches, such as Principal Components Analysis, to be used to determine elemental source fingerprints. These in turn have been applied to Chemical Mass Balance methods to completely specify relative and absolute source contributions to ambient fine particle pollution in a range of cities throughout Australia and internationally.

The average PM_{2.5} mass of between 9 and 13 $\mu\text{g}/\text{m}^3$ in the Sydney, Wollongong, Newcastle regions was composed of about 30% elemental carbon, 25% organic matter, 20% ammonium sulphate, 10 % airborne soils and 10% seaspray with the remainder being trace elements, water vapour and nitrates that are not well measured on Teflon filters. If airborne soils and seaspray are considered natural sources and all other sources were anthropogenic then between 75% and 80% of the fine particle pollution is manmade in and around Sydney.

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