ION BEAM ANALYSIS, POSITIVE MATRIX FACTORISATION AND WIND BACK TRAJECTORIES, TOOLS FOR $PM_{2.5}$ PARTICLE RESEARCH IN AUSTRALIA

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Abstract

ANSTO have performed long-term $PM_{2.5}$ particle collection and analysis at locations covering a range of demographics including urban, rural and industrial sites in Australia and Asia. As a result, ANSTO has established a uniquely extensive number of fine particl e datasets. The collected samples have been analysed using a combination of nuclear Ion Beam Analysis (IBA) techniques, positive matrix factorisat ion (PMF) and wind back trajectories (WBT). These techniques not only deter mine the quantitative concentrations of key elements in the collected aerosols, but also provide significant information on source fingerprints, sour ce contribution to total pollution on a local scale, and source long-range trans port. In addition, the analysis of long-term datasets can often reveal significant short-term aerosol events that only become evident when viewed in context of the long-term trends for that location. This paper summarises the complimentary IBA, PMF and WBT analysis methods used at ANSTO fo r extracting quantitative chemical composition and source apportionment from large $PM_{2.5}$ aerosol data sets. Specific examples resulting from long-term analysis of fine particle collected at the Wollongong, Sydney and Newcastl e sites over the past 12 years (1998 – 2010) is used to highlight each technique.

Keywords: IBA, PMF, fine particles

1. Introduction

Atmospheric particulates can range in size from nanometers to tens of microns in diameter. $PM_{2.5}$ particles have a diameter of $2.5\mu m$ and below and are commonly referred to as 'fine particles'. Fine particles can originate from both anthropogenic sources such as biomass burning and motor vehicles as well as natural sources such as sea spray and windblown soil (Cohen *et al.*, 2004b). It has been reported that fine particles can be inhaled deep in to the human resiratory system enabling direct access to the blood stream and may consequently have adverse health effects (Dockery *et al.*, 1993, Dockery & Stone, 2007). Fine particles can also have atmospheric residence times of days, or even weeks, and can be transported hundreds and/or thousands of kilometers from their source (Zhao *et al.*, 2008).

Characterising and monitoring fine particles has therefore become increasingly important for governments and regulatory bodies both in Australia and around the world. In fact, government legislation in Australia now requires Local Councils to provide regular State of the Environment (SoE) reports to Parliament on air quality (Cohen *et al.*, 2004b).

ANSTO has been involved in air borne fine particles research since the early 1990's. During this time fine particles have routinely been collected at selected urban, rural and industrial sites in Australia and Asia. This long term fine particle characterisation study is the only one of its kind taking place in Australia, and ANSTO has established a significantly large and unique data set for each sampling site.

The collected samples have been analysed at ANSTO using accelerator based Ion Beam nuclear Analytical methods (IBA) together with positive matrix factorisation (PMF) and wind back trajectory (WBT) techniques. The powerful combination of these techniques provides the ability to quantitatively determine the concentration of key elements in the aerosols (from hydrogen to lead), as well as extract significant information about source fingerprints, source contribution to total pollution on a local scale, and source long-range transport on a regional scale.

This paper highlights some of the fine particle data generated over the past 12 years (July 1998 –

December 2010). Specific examples from three demographically interesting NSW sites; Mayfield (Newcastle), Mascot (Sydney) and Warrawong (Wollongong) are used to demonstrate how each of these tools have been applied to fine particle research.

Detailed information regarding our sampling methods, IBA, PMF and WBT techniques are reported elsewhere and will therefore only be summarised in this paper for completeness (Cohen, 1998, Cohen *et al.*, 2010a, Cohen *et al.*, 2010b, Cohen *et al.*, 2004a, Cohen *et al.*, 2004b, Paatero, 2004a, Paatero, 2004b).

2. Fine Particle Sampling

$PM_{2.5}$ fine particles have routinely been collected every Wednesday and Sunday over a 24 hour period from midnight to midnight. A standard IMPROVE $PM_{2.5}$ cyclone aerosol sampler was used with 25 mm diameter, 3μm stretched Teflon filters and a flow rate of 22 L/min (Cohen *et al.*, 1996).

Since 1991 we have analysed over 30,000 fine particle filters from more than 70 sites.

3. Simultaneous Ion Beam Analysis

Accelerator-based IBA techniques: particle induced X-ray emission (PIXE), particle induced gamma ray emission (PIGE), particle elastic scattering analysis (PESA) and Rutherford Backscattering (RBS) have been applied to fine particle aerosol filters. These non-destructive IBA techniques are performed simultaneously using an 8 mm diameter 2.6 MeV proton beam with target currents ranging from 10-15nA. PIXE detects the elements ranging from Al to Pb, PIGE detects the lighter elements such as F and Na, RBS detects C, N and O and PESA detects H. The combination of these IBA techniques can therefore provide the quantitative elemental concentrations of the following key elements commonly occurring in fine particles: H, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb. The minimum detectable limits (MDL) for IBA are typically less than 10ng/m^3 of sampled air with experimental errors between ±7% for most of the elements analysed (Cohen *et al.*, 2005).

Mascot is an inner city suburb of Sydney surrounded by major arterial roads as well as the Sydney International airport. It is therefore not surprising that the $PM_{2.5}$ at that site is dominated by elements present in vehicle emissions. In 2000 the Australian government initiated a program to limit the supply and use of leaded petrol, with complete phase-out by 2002 (Cohen *et al.*, 2005). The implementation of this policy to reduce Pb from vehicles corresponds well with our IBA results for Mascot which showed a significant reduction in elemental Pb concentration at the end of 2000, followed by sustained and ongoing lower Pb levels in Figure 1. The remaining Pb measured after the cessation of leaded petrol is likely due to a combination of remnant road dust and industry sources.

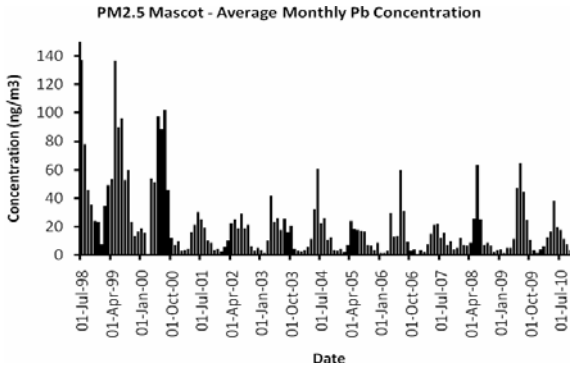


Figure 1. Long term (1998-2010) average monthly Pb concentration at Mascot (Sydney inner city site).

The elemental concentrations can also be used to estimate certain source components such as soil, sea salt and ammonium sulphate using the method reported by Malm et al. (Malm *et al.*, 1994):

$$Salt = 2.54[Na] \quad (1)$$

$$Ammonium\ Sulphate = 4.125[S] \quad (2)$$

$$Soil = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 1.94[Ti] + 2.42[Fe] \quad (3)$$

$$Smoke = [K] - 0.6[Fe] \quad (4)$$

$$Organics = 11([H] - 0.25[S]) \quad (5)$$

$$RCM = Salt + Ammonium\ Sulphate + Soil + Smoke + Organics + BC \quad (6)$$

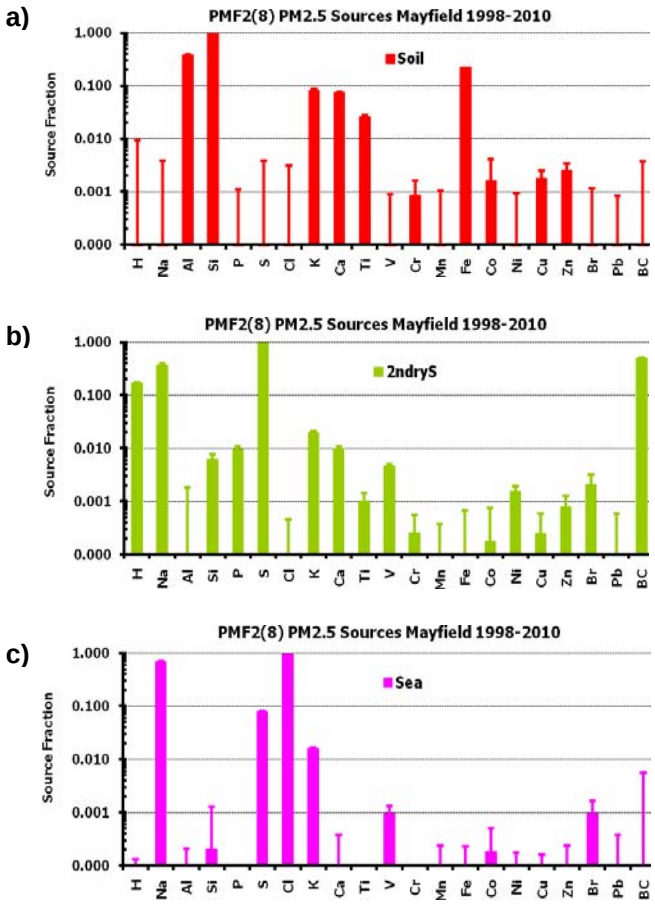
The black carbon (BC) was determined using the standard He/Ne laser absorption technique (633nm wavelength) which assumes a mass absorption coefficient of 7 m^2/g for $PM_{2.5}$ carbon particulates.

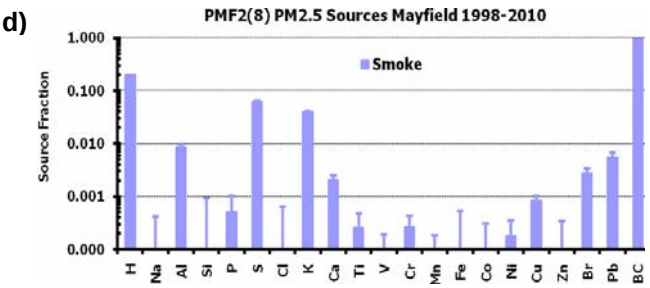
For the best source apportionment results, this method requires the reconstructed mass (RCM) from eq. (6) to be 50-150% of the gravimetric mass, known as high 'mass closure' (Cohen *et al.*, 2010a). It is important to note however that this only estimates the major $PM_{2.5}$ chemical components and is not to be confused with source fingerprints.

4. Positive Matrix Factorisation (PMF)

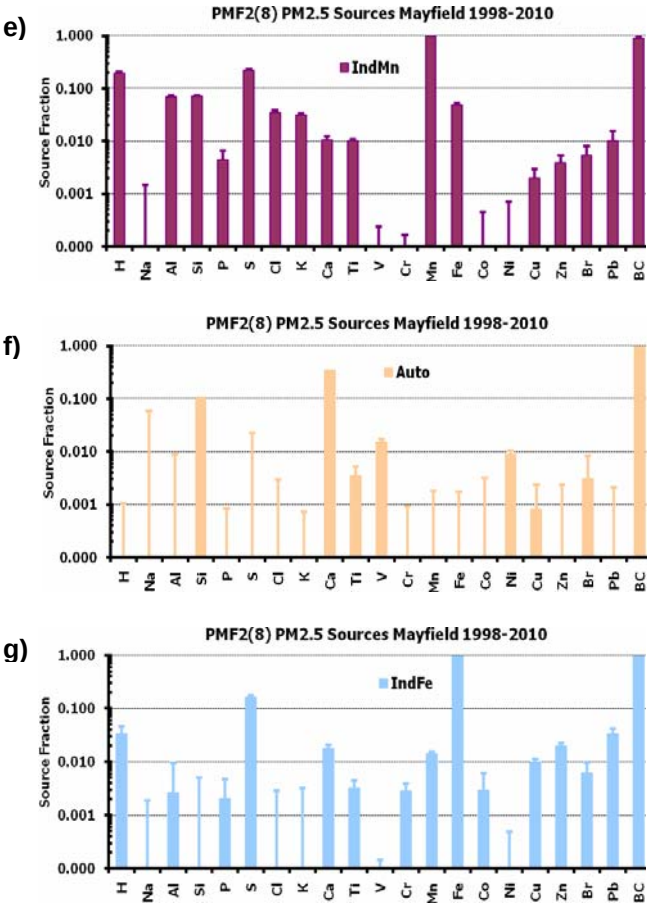
Positive Matrix Factorisation (PMF) is a statistical model which can be applied to large data-sets for identifying inter-element correlations in order to generate source fingerprints and their contribution to the total fine particle mass (Cohen *et al.*, 2010a, Liu *et al.*, 1996). PMF has been described in detail elsewhere and will not be reproduced again here (Cohen *et al.*, 2010a).

The source fingerprints determined by PMF for the Mayfield (Newcastle) site over the period 1998 – 2010 are shown in Figure 2. It should be noted that the PMF process does not automatically assign a source name to each fingerprint; this is done by the analyst based on site knowledge and experience in identifying the major elem ental contributors for each source. For example, the 'Sea' source is assigned to the fingerprint dominated by high Na and Cl concentrations and often accompanied by Si, S, K and Ca.





The 'Soil' source is typically identified by high levels of Al, Si, Ca, Ti, and Fe and can often be accompanied by K and P. The 'secondary Sulphate' (2ndryS) source contains high levels of H, S and black carbon (BC). The 'Smoke' source fingerprint is dominated by high levels of H, K, and BC. The 'Auto' source has high H, BC, S and Ni along with Al, Si and Ti likely due to road dust and P, Ca, V, Zn, Br and Pb which are elements that can be present in petrol and/or oil lubricants. Industry Zn, Fe and Mn are assigned to fingerprints characterised by high levels of Zn, Fe and Mn respectively.



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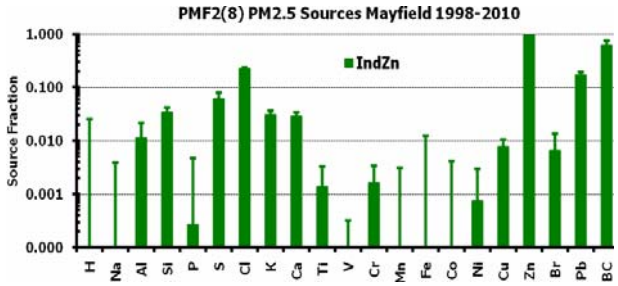


Figure 2 a) – h). PMF identified source fingerprints for Mayfield (Newcastle) Site over the period (1998-2010).

As expected,our long term results also show typical seasonal (summer & winter) variations for many of the major sources. However, changes to these long-term routine variations can sometimes highlight more specific pollution events. For example, at the industry dominated Mayfield site, the observed 'industry Mn' source (Fig. 3) showed a significant deviation from its typical long-term seasonal variation; with the measured concentration decreasing dramatically at the start of 2008. This decrease corresponds to the closure of a significant industry source of manganese in Mayfield which also occurred at the start of 2008. This known industrial operation manufactured and supplied approximately 15% of the worlds manganese dioxide, MnO_2 requirements for appplications such as alkaline dry cell batteries (Hughes, 2006).

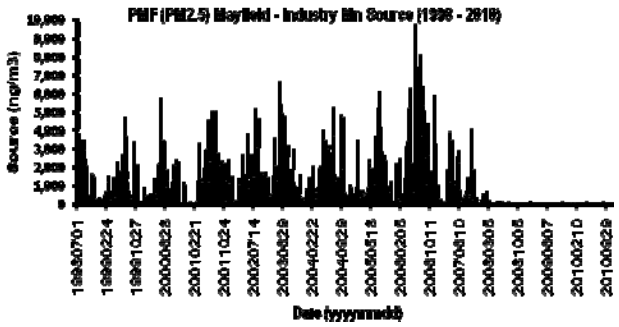


Figure 3. Concentration of PMF 'Industry –Mn' source measured at Mayfield from 1998 – 2010.

Similarly, it can be seen in Figure 4 that the 'Industry Fe' source at Mayfield showed a marked decrease at the end of 1999. It is known that industrial operations associated with the production of steel were one of the major source contributors of Fe in Newcastle. It is therefore likely that the dramatic reduction in Fe emmision observed at the Mayfield site from 1999 onwards is related to the October 1999 closure of a major industrial steel works plant in Newcastle.

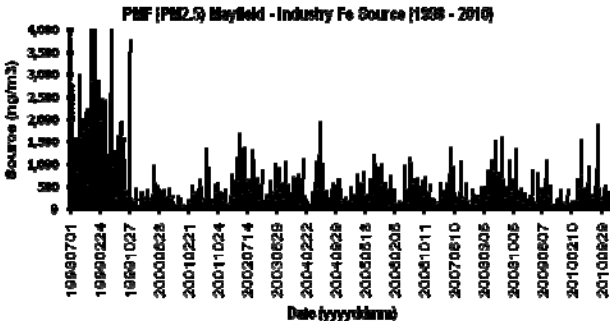


Figure 4. Concentration of PMF 'Industry-Fe' source measured at Mayfield from 1998 – 2010.

The PMF technique can also determine the relative contributions of each of the sources to the total $PM_{2.5}$ pollution at that site. For example, our analysis of Mayfield revealed approximately 79% of the fine particulate matter in the atmosphere over the last 12 year period can be attributed to anthropogenically influenced sources such as smoke, auto, industry and secondary Sulphates as shown in Figure 5. Also, by presenting fine particle data as source fingerprints and source contributions in addition to elemental concentrations, it becomes much more informative for governments, local councils and regulatory bodies.

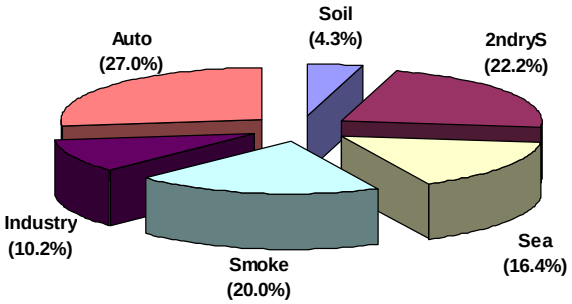


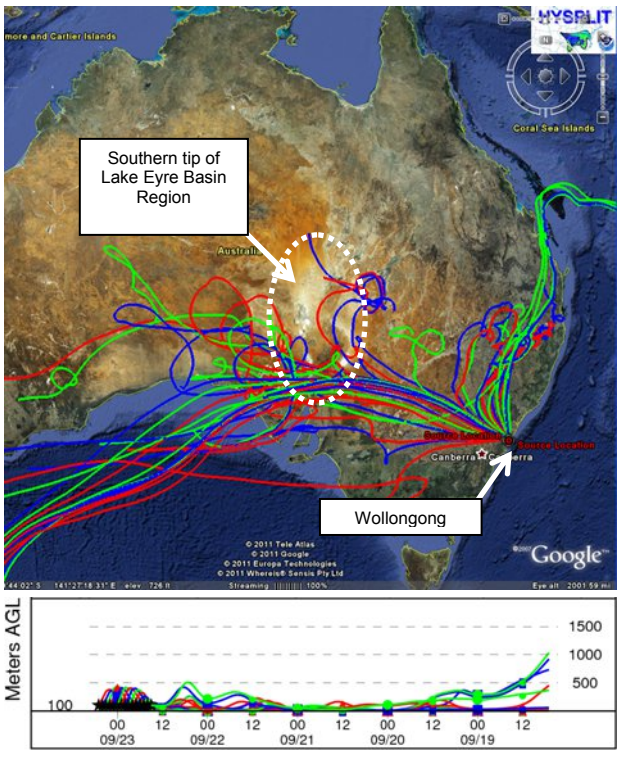
Figure 5. Percentage source contribution in Mayfield based on PMF data obtained from 1998-2010

5. Wind Back-Trajectory

Wind back-trajectory (WBT) analysis has been used for investigating results where the short-term elemental or source concentrations are significantly higher than the typically observed long-term trends for that site. For example, this was the case for extremely high soil source levels measured at Warrawong (Wollongong) on the 23 rd September 2009.

The HYSPLIT v4.0 (Hybrid Single-Particle Lagrangian Integrated Trajectory (Draxler *et al.*, 2009)) model was used to determine the wind trajectories at Wollongong 5 days backwards in time from the 23 rd September 2009. A 500 m starting height above ground level (AGL) is commonly selected in literature (Cohen *et al.*, 2010b, Dvorska *et al.*, 2009, Erel *et al.*, 2007) to ensure that the start of the trajectory is within the atmospheric boundary layer (ABL). However, compounds within the ABL may not always be evenly distributed and have been shown to increase or decrease with height (Dvorska *et al.*, 2009, Farrar *et al.*, 2005). To account for this possible variability we generated our back trajectories at starting heights of 100 m, 300 m and 500 m AGL.

Figure 6 shows the 5 day (120 hr) wind back trajectories started every hour between 00:00 – 15:00 (AEST) on the 23 rd of September 2009. The back trajectories for all three starting heights displayed distinctive swirling wind patterns over the southern tip of the arid Lake Eyre Basin region. The combination of low wind altitudes and swirling wind motion is therefore likely to have facilitated soil uptake from the Lake Eyre Basin region and transport it more than 1300 km to the eastern Australian coast.



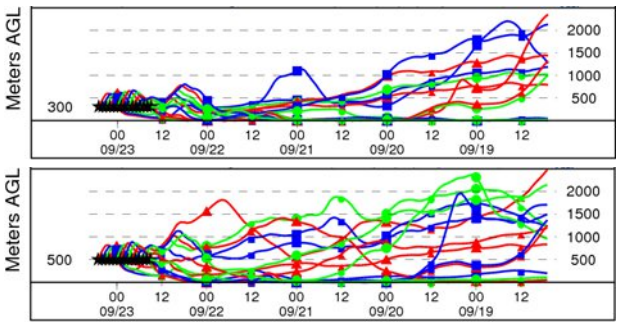


Figure 6. 120hr wind back trajectories and heights for Wollongong taken every hour between 00:00 – 15:00 (AEST) on the 23-Sep-09 for 100, 300 and 500m AGL starting heights.

6. Summary

ANSTO has amassed 12 years of 24 hour, bi-weekly (Wednesday and Sunday) fine particle sampling data sets for sites covering a range of demographic regions in Australia and Asia.

Ion beam analysis techniques have been used to quantitatively determine the concentration of 21 key elements, from H to Pb, with high sensitivity. IBA results identified a reduction of fine particle Pb in the inner city Mascot region following the Government initiative to cease leaded petrol supply in Australia.

Positive matrix factorisation has routinely been used to statistically identify both source chemical fingerprints and their contribution to the total pollution on a local scale. PMF results ascertained 8 fine particle sources contributing to pollution at Mayfield. Analysis of the long-term Industry-Mn and Industry-Fe sources revealed significant reductions that correlate well with the closure of certain industrial operations in that local area.

Wind back trajectory analysis has been used to determine the origin of PMF sources which do not otherwise conform to the typical long term trends for a site. Five day WBT analysis determined that abnormally high soil levels measured at Wollongong on the 23 rd September 2009 were due to long range soil transport more than 1300 km's from the Lake Eyre Basin region to the New South Wales coast.

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