Ion Beam Analysis and Positive Matrix Factorisation modeling; tools for exploring aerosol source fingerprints

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Abstract

ANSTO has been involved in $PM_{2.5}$ monitoring and analysis since 1991. Long term sampling together with information on concentrations of total collected gravimetric mass, black carbon and 23 elements from hydrogen to lead obtained by accelerator based nuclear analytical methods have been used for generating large data sets. The Positive Matrix Factorisation (PMF) modelling technique has been applied to these data sets for exploring $PM_{2.5}$ source fingerprints and source contributions at Sydney and Brisbane. Data in this presentation covers sources and their contributions to total $PM_{2.5}$ pollution at Liverpool (Sydney) from January 1998 to December 2006 and at Rocklea (Brisbane) from January 1998 to December 2003.

Introduction

Fine particle aerosols ($PM_{2.5}$) with aerodynamic diameter of 2.5μm and less are collected on stretched Teflon filters using cyclone-based samplers [1-2]. Samples are generally collected over a 24-hour period from midnight to midnight every Wednesday and Sunday. Collected samples are analysed by accelerator based Ion Beam Analysis techniques (IBA) using an 8mm-diameter beam of 2.6 MeV protons [3-5]. IBA includes four techniques applied simultaneously. PIXE (Particle Induced X-ray Emission) for analysis of the range of elements including Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, Br and Pb. PIGE (Particle Induced Gamma-ray Emission) for analysis of F and Na. RBS (Rutherford Back Scattering) for analysis of C, O and N and PESA (Particle Elastic Scattering) for analysis of H. On data obtained by long term sampling and IBA nuclear based analysis the Positive Matrix Factorisation (PMF) statistical receptor-modelling technique [6-10] has been applied to characterise fine aerosol particle origins (fingerprints of sources) and their contributions to the total air pollution at Liverpool (Sydney) and Rocklea (Brisbane). The Liverpool sampling site is located close to the Hume Highway in the centre of the Sydney Basin in a mixed residential and commercial area with an average annual $PM_{2.5}$ mass concentration of 8±4 $\mu g/m^3$ during 1998-2006. The Rocklea sampling site is located in an open farm surrounded by light industry and residential areas with extensive heavy vehicle and freight railway components in the traffic and with an average annual $PM_{2.5}$ mass concentration of 6±3 $\mu g/m^3$ during 1998-2003.
NOTE: The Australian National Environment Protection Council (NEPC) proposes a new National Environment Protection Measure (NEPM) for $PM_{2.5}$ particulates to be 8 $\mu g/m^3$ for the annual average concentration.

Results

For the Liverpool data 8 factors/sources were identified and are presented in Figure 1. For the Rocklea data 7 factors/sources were identified and are presented in Figure 2. Names of the factors/sources are not defined by the PMF program and are at the discretion of the user. They have been assigned by looking at the major elemental contributors in the elemental mix for each factor/source. For example the Seaspray source is characterised by a high presence of Na and Cl and can be accompanied by elements such as Si, S, K and Ca. It can also appear as chlorine depleted Seaspray which is the case at the Liverpool sampling site. The Soil source is characterised by a high presence of Al, Si, Ca, Ti and Fe and can be accompanied by K and P. The Secondary Sulphate source (2ndS) is characterised by a high presence of H, S and black carbon (BC).
The Smoke source is characterised by high presence of H, K and BC.

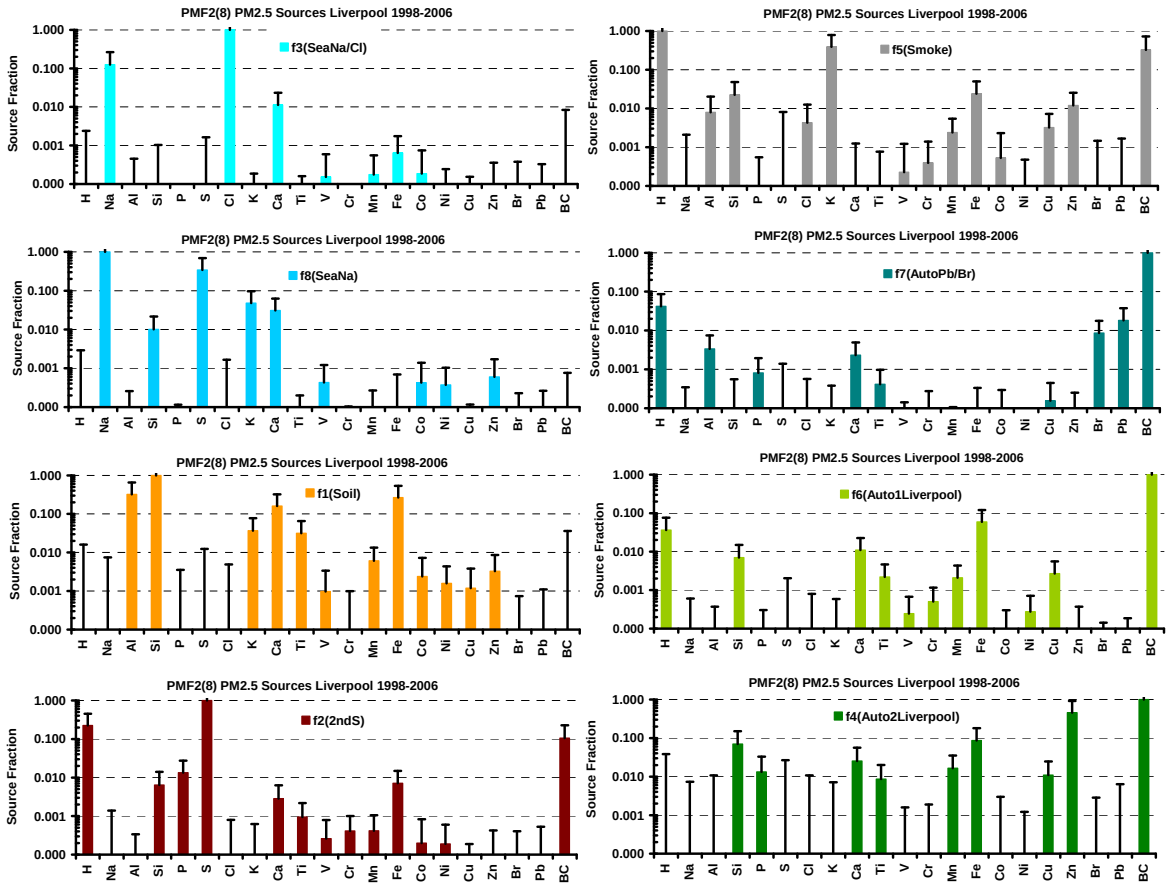

Figure1. PMF identified factors/sources for Liverpool (Sydney) site.

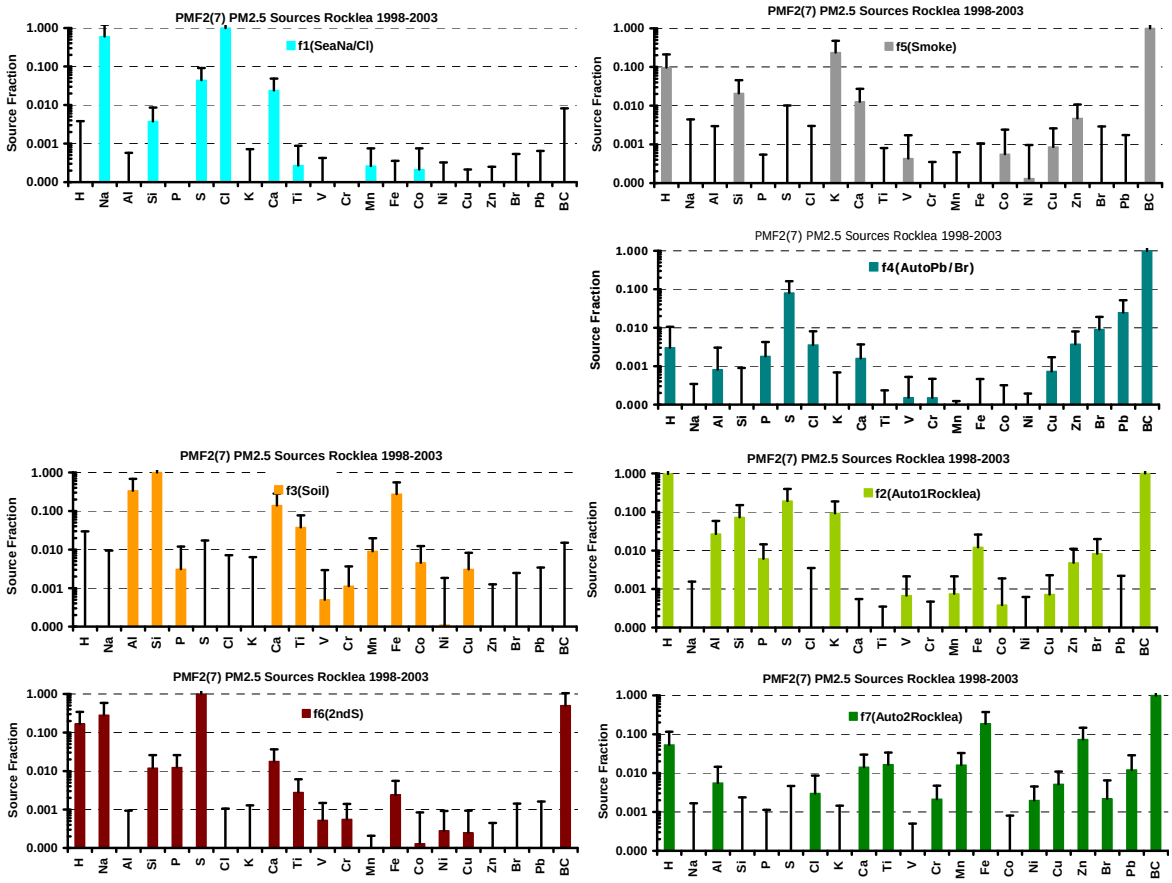

Figure 2. PMF identified factors/sources for Rocklea (Brisbane) site.

The Auto sources are characterised by a high H, BC, S and road dust components such as Al, Si and Ti, as well as components from additives in oil and lubricants such as P, Ca, V and Zn. Pb and Br are also present in Auto sources. After removal of leaded petrol from use Pb and Br are still present in the atmosphere in very small concentrations as road dust components.

The advantage of the PMF technique is that both the source fingerprints and their relative contributions to total $PM_{2.5}$ pollution can be estimated simultaneously. The percentage average source contributions for Liverpool and Rocklea sampling sites obtained by PMF analysis for five major sources are shown in Figure 3. From Figure 3. it can be seen that anthropogenic sources, Auto, Smoke and Secondary sulphate, make significant contributions to airborne particulate pollution at both sampling sites.
NOTE: Sea sources at Liverpool sampling site are combined in one source named Sea as well as Auto sources at both sampling sites.

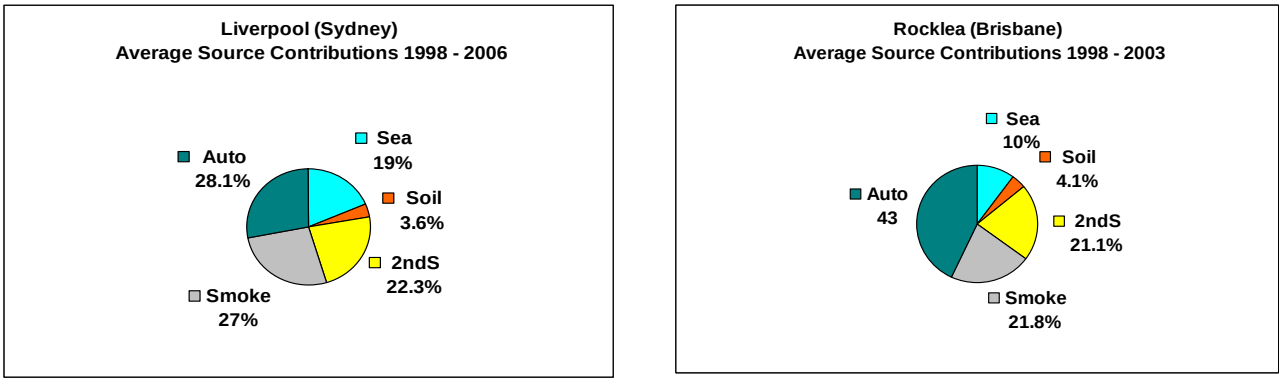

Figure 3. The percentage average source contributions at Liverpool sampling site from January 1998 to December 2006 and at Rocklea sampling site from January 1998 to December 2003.

Figures 4. demonstrates daily percentage Smoke and Soil contributions for Liverpool sampling site. From Figure 4. seasonal Smoke variations and extreme contributions of windblown Soil due to dust storm events can be seen.

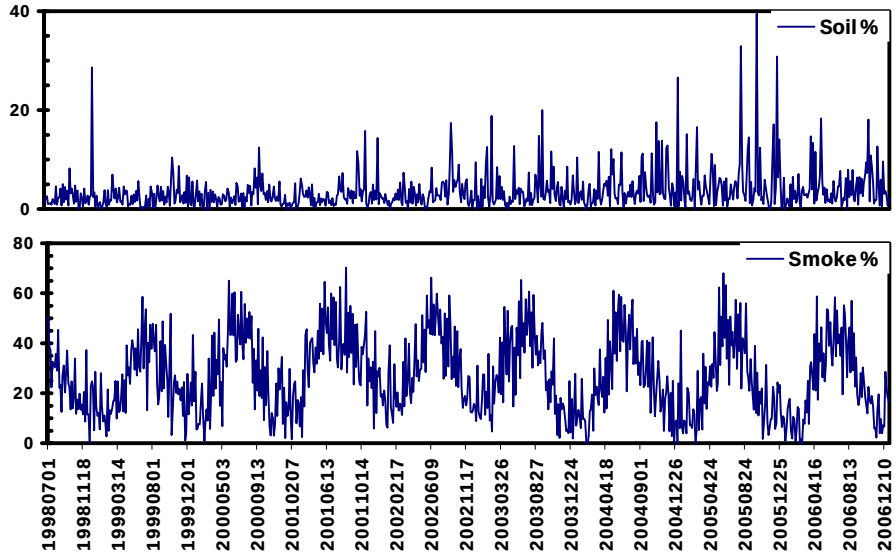

Figure 4. Daily Percentage Soil and Smoke for Liverpool.

Conclusion

IBA techniques (PIXE, PIGE, RBS and PESA) are powerful multi-elemental analytical tools in air pollution studies and, in combination with the PMF modeling technique, can provide further information on source fingerprints and their contribution to pollution.

References

[1] Malm, W. C., Sisler, J. F., Huffman, D, Eldred, R. A., Cahill, T. A. (1994) *Journal of Geophysical Research.* **99**, 1347.

[2] Cohen, D. D., Bailey, G. M., Kondepudi, R. (1996) Elemental Analysis by PIXE and other IBA Techniques and their Application to Source Fingerprinting of Atmospheric Fine Particle Pollution, *Nucl. Instr. Meth.*, **B109-110**, 218-226.

[3] Cohen, D. D., (1999a) Accelerator Based Ion Beam Techniques for Aerosol Analysis. In Elemental Analysis of Airborne Particles. S. Landsberger and M. Creatchman (eds.) *Gordon Breach Science Publishers.*

[4] David D. Cohen, Ed Stelcer, Olga Hawas, David Garton, IBA Methods for Characterisation of Fine Particulate Atmospheric Pollution: A local, regional and global research problem. *Nucl. Instr. and Methods* **B219-220** (2004) 145-152.

[5] David D. Cohen, David Garton, Eduard Stelcer, Olga Hawas, Accelerator Based Studies of Atmospheric Pollution Processes. *Radiation Physics and Chemistry*, **71** (2004) 759-767.

[6] Lee E., Chan C. and Paatero P. 1999, Application of positive matrix factorisation in source apportionment of particulate pollutants in Hong Kong, *Atmospheric Environment*, **33**, 3201-3212.

[7] Paatero P. 2004, User's Guide for Positive Matrix Factorisation Programs PMF and PMF2. *YP-Tekniika KY Company*.

[8] Andrew Chan, Rod Simpson, David Cohen, Olga Hawas, Eduard Stelser, Lyn Denison, Neil Wong, Gary Golding, Elizabeth Christenson, Willy Gore, Mary Hodge, Eva Comino, Stewart Carswell, Apportionment of Sources of Emission of Particles in Four Major Australian Cities by Positive Matrix Factorisation. *Proceedings of 17th International Clean Air Conference, Hobart, Tasmania, Australia*, 3-6 May 2005.

[9] B. A. Begum, S.K. Biswas, P. K. Hopke, D.D. Cohen, Multi-elemental analysis and characterisation of atmospheric particulate pollution in Dhaka. *Aerosol and Air Quality Research*, **6** (2006) 334-359.

[10] David D. Cohen, Eduard Stelcer, Vuong Thu Bac, Quantification of Fine Particle Composition, Sources and Transboundary Transport in Hanoi, Vietnam from 2001-06.*14th World Congress, 18th CASANZ Clean Air Conference, Brisbane, QLD, Australia*, 9-13 September 2007.