



# Ion beam methods to determine trace heavy metals concentrations and sources in urban airsheds

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## Abstract

Unique data for Australia on the concentration of selected metals in fine particle ambient air pollution is presented for urban, industrial and rural sites along 300 km section of the eastern coast line of Australia around Sydney. IBA techniques were used to determine over 25 different chemical species in the air including, H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Se and Pb. This included many trace metals at concentrations around 1 ng/m<sup>3</sup> of air sampled. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Internationally interest in fine particle (<2.5 μm diameter) air pollution in urban and global environments has increased significantly over the past decade [1–6]. The ion beam techniques of PIXE, PIGE, RBS and forward recoil analysis (FRA) [2,3] are now routinely used to determine the composition of fine particle pollution in urban airsheds. These IBA techniques can determine over 25 different chemical species in air [1–4,6] including, H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Se and Pb. Many trace metals at concentrations around 1 ng/m<sup>3</sup> of air sampled can be determined. Filter papers used to collect these samples, of only a few hun-

dred micrograms, are essentially thin targets for IBA analysis and well suited to the method. This paper reports on a unique data set, of nine years of fine particle concentrations, obtained using these four simultaneous IBA methods on filters collected at urban, rural and industrial sites in NSW, Australia. The heavy metal concentration variations with time and season are reported for the first time for urban and industrial airsheds in Australia. Also, because of the large number of chemical species determined by these IBA methods it was possible to statistically associate many trace metal pollutants directly with selected anthropogenic sources, such as industry, automobiles and biomass burning [6–8].

## 2. Sampling sites, filters and IBA characterisation

Since 1992 we have been sampling fine particles every Wednesday and Sunday for 24 h at selected

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urban, rural and industrial sites in New South Wales on the eastern coast of Australia. Fig. 1 shows the four sites discussed here. They are about 100 km apart. Warrawong and Mayfield are industrial sites, on the coast strongly influenced by steel production and heavy industry. The Mascot site is an urban site in the centre of Sydney and strongly influenced by motor vehicle traffic, whereas Crookwell is a rural site in the centre of a farming district, not immediately affected by roads or industry. Crookwell, however, has the potential to be affected by long range fine particle pollution transport from coal fired power stations at Lithgow to the north and urban and industrial pollution from Wollongong to the east and Sydney to the north east.

Samples for IBA analysis were collected on 25 mm diameter stretched Teflon filters approximately 230  $\mu\text{g}/\text{cm}^2$  thick. An 8 mm diameter, 10 nA beam of 2.6 MeV protons was used to simultaneously obtain PIXE, PIGE, RBS and FRA spectra as described previously [2,3,7]. A typical PIXE spectrum, obtained for 3  $\mu\text{C}$  of charge, from the urban Mascot site is shown in Fig. 2. The extensive range of elements from Al to Pb is clearly visible, including many of the key metals of interest. The graph is a log plot covering four decades of concentration from a few percent to several  $\mu\text{g}/\text{g}$ .

The spectra peak areas were extracted and converted to concentrations using the standard routines for each of the Teflon filters collected at each site over the full nine year study period. As

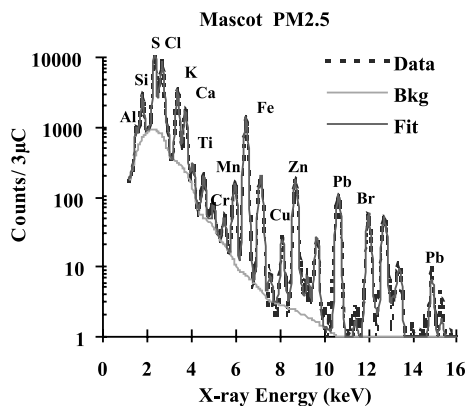


Fig. 2. A typical PIXE spectrum for a 24 h fine particle sample from the urban Mascot site.

the targets were thin, concentrations were typically obtained in  $\text{ng}/\text{cm}^2$  on the filter. This was converted to  $\text{ng}/\text{m}^3$  of air sampled by multiplying by the exposed filter area (2.27  $\text{cm}^2$ ) and dividing by the volume of air sampled in 24 h (32  $\text{m}^3$ ). Minimum detectable limits below 1  $\text{ng}/\text{m}^3$  were readily obtainable for trace metals from Ti to Zn [2,3].

### 3. Seasonal concentrations and variations

The sampling time for this study was sufficiently long to obtain daily, monthly, seasonal and annual averages for each element in the range discussed above. Table 1 shows the nine year average concentrations of a range of elements, including metals of interest, for the Warrawong, Mascot and Mayfield sites and the two year averages for the rural site at Crookwell. The equivalent annual average PM2.5 fine particle masses for each of these sites were  $(8.2 \pm 5)$ ,  $(10.1 \pm 7)$ ,  $(11.4 \pm 6)$  and  $(3.8 \pm 1.7)$   $\text{ng}/\text{m}^3$  respectively.

The low concentrations measured at the Crookwell site, for most elements, reflects the clean nature of the ambient air there. Indeed these long term average concentrations were lower, in some instances than equivalent concentrations measured at a remote global baseline station at Cape Grim in North Western Tasmania [7]. Anthropogenic metals V, Cr, Co, Ni and Cu were generally below 10  $\text{ng}/\text{m}^3$ , whereas Zn and Pb, associated with motor vehicles and industry, were

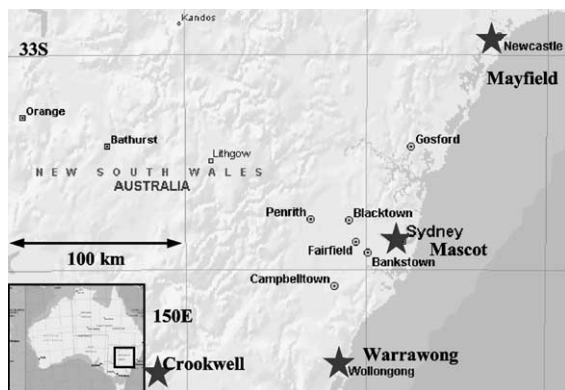


Fig. 1. Map of the east coast of Australia showing the location of the four fine particle sampling sites (★).

Table 1

The nine year average fine particle (PM<sub>2.5</sub>) concentrations (ng/m<sup>3</sup>) of selected elements and metals at the four study sites on the eastern coast of Australia

Element	Warrawong 1992–2000 (ng/m <sup>3</sup> )	Mascot 1992–2000 (ng/m <sup>3</sup> )	Mayfield 1992–2000 (ng/m <sup>3</sup> )	Crookwell 1992–1993 (ng/m <sup>3</sup> )
Al	29 ± 15	45 ± 43	59 ± 27	14 ± 8
Si	69 ± 33	76 ± 48	121 ± 46	39 ± 24
Ti	5 ± 3	5 ± 3	9 ± 5	1.2 ± 0.8
V	1.2 ± 0.7	1.1 ± 0.5	1.5 ± 0.7	0.2 ± 0.1
Cr	1.4 ± 1	1.1 ± 1.1	0.9 ± 0.5	0.3 ± 0.1
Mn	7 ± 3	9 ± 14	130 ± 82	0.4 ± 0.2
Fe	260 ± 136	98 ± 82	451 ± 292	10 ± 7
Co	1.3 ± 0.7	0.4 ± 0.3	2.1 ± 1.5	0.2 ± 0.1
Ni	0.8 ± 0.7	1.1 ± 1.2	1.1 ± 1.8	0.3 ± 0.2
Cu	45 ± 7	5 ± 3	5 ± 4	0.6 ± 0.8
Zn	36 ± 26	29 ± 25	86 ± 43	1.2 ± 0.8
Br	13 ± 11	59 ± 78	18 ± 13	1.4 ± 0.5
Pb	48 ± 38	151 ± 166	71 ± 44	3.3 ± 2.1

significantly higher at all sites compared to the rural Crookwell site.

Although the values in Table 1 were generally low by world standards, there were strong long term, seasonal and monthly variations for many elements. Fig. 3 shows the monthly average values for Pb at the urban Mascot site strongly affected by motor vehicles.

Two distinct trends are obvious, firstly the summer winter variation, with winter being 4–6 times larger and, secondly, the fall in winter maxima and summer minima with time as the lead additives in Sydney petrol were progressively reduced from 1994 onwards.

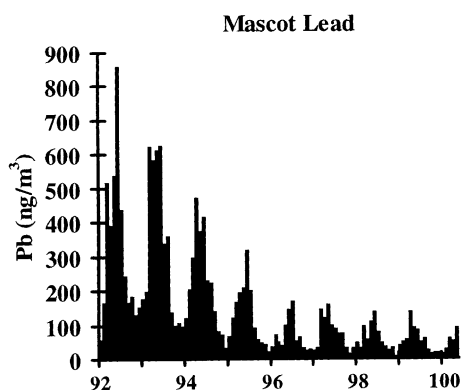


Fig. 3. Plot of the fine particle Pb content in ambient air at Mascot from 1992 to 2000.

Other elements also showed some seasonal variations, for example, Co at the industrial site of Mayfield, north of Sydney, as shown in Fig. 4. Here fine particle Co is 3–5 times higher in the summer than the winter and there is no apparent long term trend from 1992 to 2000.

At the industrial sites affected by steel production, such as Warrawong, Co and Fe were strongly correlated, as shown in Fig. 5, demonstrating that they originate from the same source most of the year round.

Similar correlations were obtained for Al and Ti with Si from airborne soil and Pb and Br from petrol driven cars. Some elements have obvious

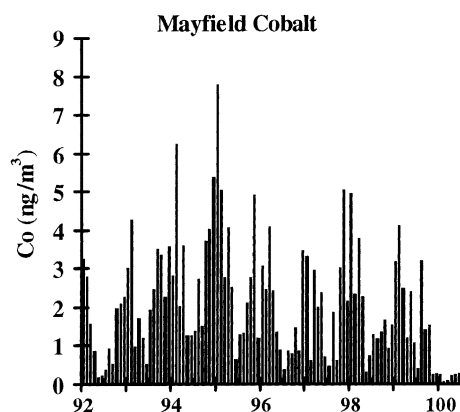


Fig. 4. Plot of the fine particle Co content in ambient air at Warrawong from 1992 to 2000.

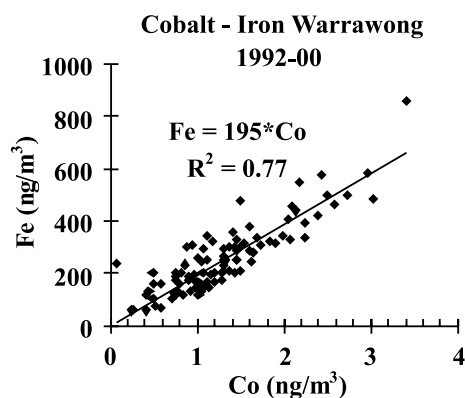


Fig. 5. Plot of average monthly Fe versus Co concentrations for the industrial site at Warrawong for the study period from 1992 to 2000.

sources, like Na and Cl in seaspray and Al and Si in soils and these obviously produce good two dimensional correlations.

#### 4. Sources of trace metals in air

Plotting one element against another can only find correlated pairs associated with the one source. A better, less biased way, to determine inter-elemental associations is by using multidimensional statistical methods such as principal components analysis (PCA), factor analysis or more recently positive matrix factorisation techniques [3,6,8–10]. Typically these techniques will identify 6–8 key factors from 25 to 30 dimensional space spanning all elements measured. In many instances these key factors can be associated with generic sources and key elemental fingerprints established for each of these sources [2,3,6]. We have applied PCA techniques to our fine particle trace element data set for the four sites used in this study. The data set contained over 3000 samples and required five factors to explain about 72% of the variance. These five factors or principal components can be ascribed to four generic fine particle sources: industry (Factors 1 and 5), motor vehicles or cars (Factor 2), soil (Factor 4) and seaspray (Factor 5). Table 1 elements linked to these four generic sources are given in Table 2.

Table 2

Elements associated with the four generic fine particle sources in the Sydney region

Elements associated with generic sources using PCA	
Industry	K, Si, Co, Fe, Ca, Cr, S, Cu, P, Zn, Ni
Cars	Br, Pb, K, Al, Si, Ti, Zn
Soil	Al, Si, Ti, Mn, Zn
Seaspray	Na, Cl, V

Fig. 6 shows how this elemental separation is achieved using PCA techniques. The industry loadings (Factor 1) were plotted against the motor vehicle loadings (Factor 2). The remaining three factors were not shown. It clearly demonstrates the industry source (Fe, Co, Ca, Cr, S, K) with high Factor 1 loadings and low Factor 2 loadings and the motor vehicle source (Pb, Br, H and C) with high Factor 2 and low Factor 1 loadings.

The (Al, Ti, Si) soil group appeared separated from both these Factors, as it was more strongly associated with Factor 3 which was not plotted. The Group (Cl, Na, Mn, Ni, Zn, V and Cu) clustered near the origin had low Factor 1 and Factor 2 loadings and were more closely linked with remaining Factors 3–5 not plotted here.

All of these elemental associations were quite expected and generally very logical except for V with a factor loading of 0.73 being strongly associated with the generic seaspray source of Factor 4. V was usually associated with cars or industry and the only explanation we can provide is that the three urban and industrial sites of Warrawong, Mascot and Newcastle were all coastal sites, being less than 1 km from the coast. The seaspray

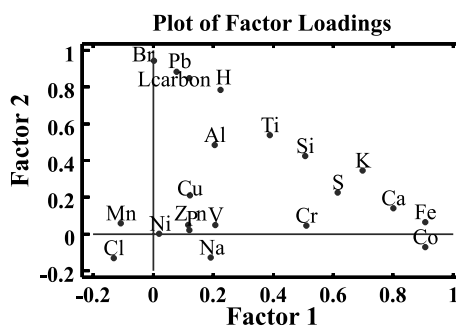


Fig. 6. Plot of PCA Factor 1 (industry) against Factor 2 (cars) loadings for all data at study sites.

component of the fine particles at these sites was typically 10–15% being higher in the summer than the winter months. This correlated strongly with the industrial sulphur based sources and may account for the somewhat odd apparent association of V with seaspray elements Na and Cl.

## 5. Summary

Ion beam analysis techniques have been used to determine regional and seasonal concentrations of major and trace metals in fine particle ambient air in airsheds in several Australian cities. Concentrations equivalent to 1 ng/m<sup>3</sup> of air sampled were readily measured on thousands of filters with a total mass of only a few hundred µg per sample. The major sources of these metals were anthropogenic and natural, being related to industrial combustion process, motor vehicle emissions, seaspray and windblown soils.

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## References

- [1] W.C. Malm, J.F. Sisler, D. Huffman, R.A. Eldred, T.A. Cahill, *J. Geophys. Res.* 99 (1994) 1347.
- [2] D.D. Cohen, G.M. Bailey, R. Kondepudi, *Nucl. Instr. and Meth. B* 109 (1996) 218.
- [3] D.D. Cohen, *Nucl. Instr. and Meth. B* 136 (1998) 14.
- [4] E. Swietlicki, K. Kemp, P. Wahlin, J. Bartnicki, L. Jalkanen, R. Krejci, *Nucl. Instr. and Meth. B* 150 (1999) 322.
- [5] Determination of Metals in Ambient Particulate Matter using PIXE, USEPA Report, EPA/625/R-96/010a, US Environmental Protection Agency, Cincinnati, OH 45268, June 1999.
- [6] D.D. Cohen, Seasonal and regional variations in ambient fine particle concentrations and sources in New South Wales, Australia: A seven year study. in: *Proceedings of International Congress of Biometeorology and International Conference on Urban Climatology*, Sydney, Australia, 8–12 November, 1999, p. 607.
- [7] D.D. Cohen, D. Garton, E. Stelcer, *Nucl. Instr. and Meth. B* 161 (2000) 775.
- [8] P.K. Hopke, *Receptor Modelling for Air Quality Management*, Elsevier Science, Amsterdam, 1991.
- [9] P. Paatero, U. Tapper, *Environmetrics* 5 (1994) 111.
- [10] P. Paatero, *Chemomet. Intell. Lab. Syst.* 37 (1997) 23.