

Multi-elemental Methods for Fine Particle Source Apportionment at the Global Baseline Station at Cape Grim, Tasmania.

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Abstract

Ion beam analysis (IBA) methods have been used for several decades now to characterise atmospheric fine particles collected on thin filter papers. The methods are multi-elemental, sensitive and very fast enabling hundreds of filter papers to be analysed. Recently, ambient atmospheric aerosols have been shown to play a significant but not well understood role in global climate forcing. This has led to a shift of fine particle analyses from the common urban airshed around major cities to airsheds more representative of global air quality. This paper discusses the use of four standard IBA methods to quantify and characterise fine particles (PM_{2.5}) collected at the global baseline station at Cape Grim in north western Tasmania over the period 1992-98.

Introduction

Fine atmospheric particles have been found to play a key roll in global climate change, pollution transport and more recently in human health [1,3]. To better understand the contributions fine particles make to these key areas it is necessary to quantify, characterise and understand seasonal variations of both the natural and the anthropogenic components on a local, regional and global scale.

Fine particles in the atmosphere influence the radiation balance of the earth in two ways, directly, by scattering and absorbing radiation and indirectly by modifying the optical properties, amount and lifetime of clouds. The effect of inhomogeneously distributed anthropogenic atmospheric fine particles is negative radiative forcing, tending to cool the earth's surface. The Intergovernmental Panel on Climate Change (IPCC) stated that size, shape, spatial distribution and chemical composition of tropospheric particles are largely uncertain [1]. Key anthropogenic particles associated with climate forcing mechanisms include elemental carbon, sulfates and soils from motor vehicles, fossil fuel combustion and biomass burning.

Accelerator based ion beam analysis (IBA) methods of particle induced X-ray emission (PIXE), particle induced γ -ray emission (PIGME), particle elastic scattering (PESA) and Rutherford backscattering (RBS) are ideally suited to determine up to 35 different elements from hydrogen to lead that are present in fine particulate samples [4-7]. These samples are typically only a few hundred micrograms of fine dust collected on inert filter papers. The determination of so many different chemical species allows for good "mass closure", where close to 100% of the measured mass can be accounted for. This good mass closure in turn allows for excellent source fingerprinting and hence reliable source apportionment calculations.

We have been collecting data on fine particles at the isolated global baseline station at Cape Grim, north western Tasmania, Australia since 1991. IBA methods at ANSTO have been used to determine four unique source fingerprints from 20 different chemical species contributing to the fine particle mass. This paper discusses the advantages of the IBA methods used, the source fingerprints identified, their seasonal variations and the interpretations made regarding the transport of pollution over hundreds and even thousands of kilometres from continental Australia and from the large southern oceans.

For the purposes of this study we define *fine particles* as all that particulate matter (PM) with aerodynamic diameters less than 2.5 μm . This is sometimes referred to as PM_{2.5}. Similarly PM₁₀ refers to all particulate matter with diameters less than 10 μm . *Coarse particles* are generally defined as particulate matter with aerodynamic diameters between 2.5 μm and 10 μm , that is the particulate fraction of the PM₁₀ above PM_{2.5}.

Cape Grim Sampling Regimes

Cape Grim is at the north western tip of Tasmania, an island about 200 km south of the main continental Australia, see Fig. 1. It has a latitude of 40° 41' S and a longitude of 144° 41' E.

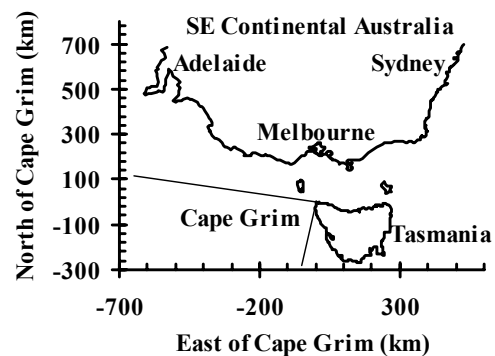


Fig. 1. The Cape Grim sampling site in Tasmania

The quadrant defined by the sector 190° to 280° about the Cape Grim site (see solid lines on Fig.1) is known as the Baseline sector as it defines a region of the globe that contains very little but the Southern Ocean for thousands of kilometres to the west and south. The region from 280° to 90° represents the Australian Continental sector and the remaining sector from 90° round to 190° is known as the Tasmanian sector. Hourly wind data collected at the Cape Grim site showed that the wind blows from the Baseline, Continental and Tasmanian sectors about 45%, 35% and 20% of the time respectively, with average wind speeds in excess of 25 km/hr. Cape Grim is an apt name for this site.

Fine particles (PM2.5) are being sampled at Cape Grim using a cyclone sampler with a 50%, 2.5 µm diameter, cutoff point for a flow rate 22 L/min. The site is positioned at the top of a 90m cliff facing the Southern Ocean. Samples are collected on 220 µg/cm² thick stretched Teflon filters of 25 mm diameter. Two 24 hour samples per week are obtained, one every Wednesday the other every Sunday. The total mass of fine particles collected on these filters is of the order of 100 µg/cm² or less. After exposure the filters are sealed in boxes and posted to ANSTO for IBA analysis.

IBA Methods

The thin stretched Teflon filters used are ideal targets for IBA analysis using 2.6 MeV proton beams from a 3 MV Van de Graaff accelerator [5-7]. Typically the proton beam loses less than 40 keV in traversing both the 100 µg/cm² of material and the 220 µg/cm² of filter. Beam diameters of around 10 mm and beam currents generally less than 15 nA were used. Full analysis was usually performed with run times corresponding to a total charge collection of only 3 µC. A hundred samples can easily be run in day.

The four IBA methods used simultaneously have been described in detail previously [5-7]. PIXE is used to determine elements from Al to Pb, PIGE light elements such as Al, F, and Na, PESA for total hydrogen analysis and RBS for total C, N and O analysis. Hence at least 20 different elements from H to Pb are determined for each filter. Each IBA technique was calibrated absolutely against known (±5%) Micromatter Standards [7] and each elemental concentration was determined to between 5 and 15%. Minimum detectable limits range from 10 to 150 ng/cm² which corresponds to about 1-10 ng/m³ of air sampled for most elements.

At the Cape Grim site elemental carbon corresponds to about 5% of the total PM2.5 fine mass and was measured using a HeNe laser and standard laser integrated plate methods LIPM [8] with a mass attenuation coefficient for elemental carbon of 7m²/g.

Results and Discussion

The data analysed here covers the period from July 1992 to December 1998. Cape Grim is a global baseline station and the range of concentrations of chemical species measured was therefore typically much lower than would be found in an urban or industrial airshed. For example, the seven year average PM2.5 mass at Cape Grim was (6.2±3.4) µg/m³ compared with typical inner city urban annual averages in Australia of between 10 and 15 µg/m³.

Table 1 shows the seven year average concentrations in (ng/m³) of air sampled for the sampling period 1992-98, together with the minimum and maximum values, for all chemical species measured by IBA methods. The average volume sampled was about 31 m³ and the filter area was 2.27 cm² giving a conversion factor of about 14 to convert these values to ng/cm² on the filter.

Species	7 year average 1992-98	Min and Max
Mass (µg/m ³)	6.2±3.4	0.91 to 22
H (ng/m ³)	108±89	5 to 1040
Na (µg/m ³)	1.0±0.9	0 to 4.9
Al (ng/m ³)	15±72	1 to 1010
Si (ng/m ³)	13±20	2 to 240
P (ng/m ³)	2±2	0 to 19
S (ng/m ³)	234±140	36 to 1440
Cl (µg/m ³)	1.5±1	0.01 to 5.6
K (ng/m ³)	39±22	4 to 190
Ca (ng/m ³)	38±25	4 to 240
Ti (ng/m ³)	1±1	0 to 19
V (ng/m ³)	1±2	0 to 14
Cr (ng/m ³)	<0.1	0 to 1.6
Mn (ng/m ³)	0.7±1	0 to 47
Fe (ng/m ³)	4±7	0 to 47
Co (ng/m ³)	<0.2	0 to 1
Ni (ng/m ³)	0.4±0.6	0 to 6
Cu (ng/m ³)	1.4±4	0 to 59
Zn (ng/m ³)	1.2±2.6	0 to 36
Br (ng/m ³)	2.6±2.4	0 to 14
Pb (ng/m ³)	1.1±1.9	0 to 18
Elt.C (ng/m ³)	332±204	37 to 1890
nss S (ng/m ³)	142±140	0 to 1410
nss-K (ng/m ³)	2.3±22	0 to 167
Seasalt (µg/m ³)	3.0±2.2	0.2 to 13
Soil (ng/m ³)	139±220	24 to 2850
Organic (ng/m ³)	540±810	0 to 9630

Table 1. PM2.5 composition averaged over 7 years.

Also shown in Table 1 are estimates of non-seasalt sulfur (nss-S), non-seasalt potassium (nss-K), seasalt

(NaCl), fine wind blown soil (oxides of Al, Si, Ti, Ca and Fe) and organic matter (H, C and O), these were obtained using the formalism of Malm et al [9]. These chemical species were included, as they are key elements in identifying natural as well as anthropogenic source contributions [6].

The large standard deviations associated with these measurements were a result of the seasonal variations in the fine particle composition not errors in the IBA measurement techniques. This is clearly shown in Figs 2 and 3, where monthly averages from the daily data are plotted from July 1992 to December 1998 for major elements sodium and nss-S respectively. Indeed during the seven year study period the annual variations for all elements were considerably less than the seasonal variations (summer to winter) demonstrated in figures.

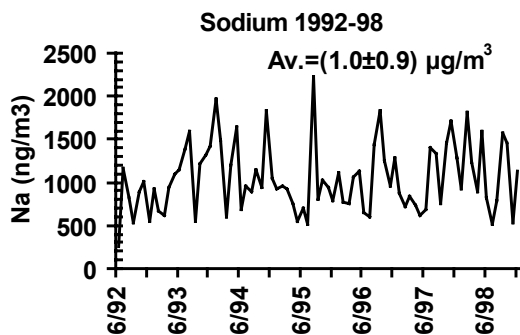


Fig. 2. Average monthly fine particle sodium concentrations for Cape Grim.

Sodium was strongly associated with seasalt and nss-S with industrial sources. The nss-S data of Fig. 3 shows the six peaks associated with summer highs and the 7 troughs associated with winter lows during the seven year sampling period. The summer peaks are typically five times the winter lows showing the importance of long term records for this type of study.

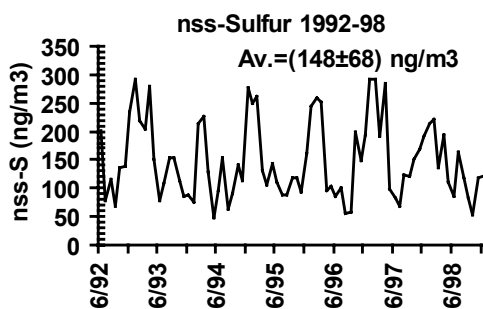


Fig. 3. Average monthly fine particle non-seasalt sulfur concentrations for Cape Grim.

Cape Grim Elemental Fingerprints

By measuring so many different elemental species for filters collected over such a long period of time it is possible to test for elemental associations and

correlations. This can be done on an element by element basis [6,7] or by the use of standard statistical procedures such as Principal Components Analysis (PCA) [10].

Table 1 shows that seasalt estimate as defined by NaCl represented about 48% of the total fine mass over the study period. Previous plots by us of the sodium versus chlorine concentrations (see Ref [6] Fig. 4) showed that most of the chlorine at Cape Grim was associated with sodium and hence originated from the seaspray source. Furthermore, the average non-seasalt sulfur was about 61% of the total sulfur (see Table 1) demonstrating that there are at least two sources of sulfur, seaspray and industry. This is well demonstrated in Fig. 4 where sodium versus sulfur is plotted for over 550 points at the Cape Grim site during the study period.

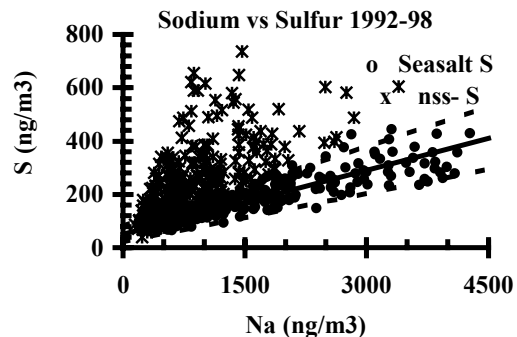


Fig. 4. Sodium versus total sulfur at Cape Grim. Full dots are seasalt sulfur and the crosses are non-seasalt sulfur.

There are two distinct groups of points, those that follow the $[S/Na] = 0.08$ line (full dots, solid line) and those that lie above this line and outside the tramlines (dashed lines) set by (0.08 ± 0.02) . The generally accepted value $[S/Na] = 0.084$ for seawater defines the range of sulfur associated with seaspray whereas all crosses outside the dotted tram lines show excess sulfur not associated with seaspray, ie possible anthropogenic sources of sulphur. There are several such sources known to be along the northern coast of Tasmania to the east of Cape Grim as well as the large urbanised city of Melbourne (2 million people) 200 km to the north of Cape Grim on the continental mainland.

The nss-K generally has two sources, soil and smoke. Table 1 shows that potassium not associated with seaspray represents about 6% of the total fine potassium, of this 13% we estimate that on average about half of the nss-K is associated with the fine soil component. Hence, on average, most of the fine potassium is related to the seaspray source. The maximum concentration of $K = 190 \text{ ng/m}^3$ in Table 1 shows that there were occasions when large fractions of the total K were not associated with seaspray. Fig. 5 shows a plot of the total fine potassium against the

total sodium concentrations. There was a good correlation between K and Na for the bulk of the points with the average $[K/Na] = (0.032 \pm 0.005)$. This compared well with the expected $[K/Na] = 0.036$ for seawater demonstrating that on average most of the K is associated with the seaspray source. There are however about 5% of the points which have significantly high K not associated with Na. Some of these have K concentrations more than four times the seven year average of $K = (39 \pm 22) \text{ ng/m}^3$. These events were associated with smoke from biomass burning and log fires in the winter which are known to be high in fine potassium.

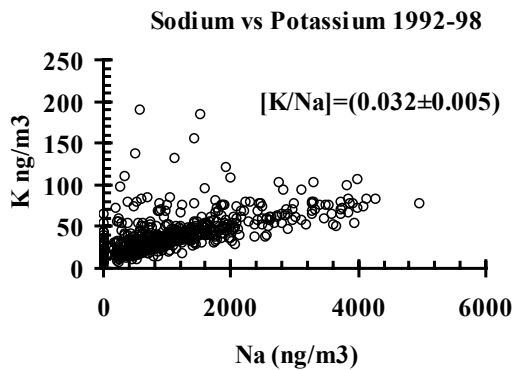


Fig. 5. Sodium versus total fine potassium at Cape Grim.

Other expected element-element correlations can be found in the data at Cape Grim. For example, silicon and aluminium were expected to be related through the airborne soil source. Fig. 6 is a plot of aluminium versus silicon. There are over 650 points in this plot with the vast majority having Al and Si concentrations less than 50 ng/m^3 and $[Al/Si]$ ratios much less than unity.

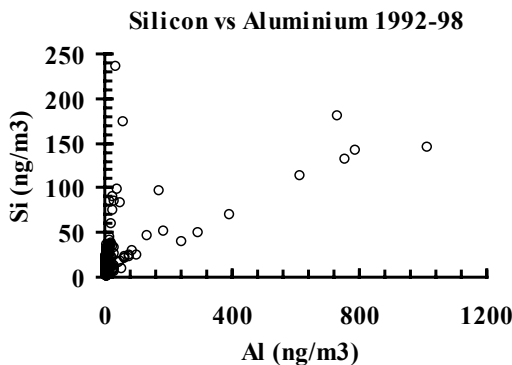


Fig. 6. Total aluminium versus silicon at Cape Grim showing two distinct source groups on with $[Al/Si] < 1$ and the other with $[Al/Si] > 1$.

There were however, another group of select points with very high Al concentrations ($> 100 \text{ ng/m}^3$) which had $[Al/Si]$ ratios much greater than unity. Inspection of the wind data showed that these events were associated with back trajectories which passed over a major aluminium smelting plant at Portland on

the Australian mainland over 400 km NW of Cape Grim between Adelaide and Melbourne. Clearly demonstrating the ability of fine particles to be transported hundreds of kilometres in a 24 hour period.

There are many possible inter-element associations such as Na and Cl from seaspray, Al and Si from windblown soil, K and elemental carbon from smoke and biomass burning or Pb and Br from leaded petrol. A much more mathematical approach is to use standard statistical methods such as Factor Analysis (FA) or Principle Components Analysis (PCA) [10]. These methods prove to be superior when large numbers of samples and many different chemical species are available. PCA methods run across our Cape Grim data set containing over 650 filters with 20 different independent chemical species (listed in Table 1) showed that generally four factors were required to explain a large percentage of the total variance. These four factors were associated with selected elements that identified them with possible fine particle fingerprints or sources at Cape Grim. The fingerprints and their elements are given in Table 2.

Fingerprint	Elements associated with fingerprints at Cape Grim
Smoke	H, P, Cl, K, Ca, Mn, Elt.C
Soil	Al, Si, K, Ca, Ti, Mn, Fe
Seaspray	Na, S, Cl, K, Ca, Br
Industry	H, P, S, V, Cr, Ni, Cu, Zn, Elt.C, Pb

Table 2. Elements identified by PCA methods as being associated with the four key fine particle source fingerprints at Cape Grim.

These four fingerprints are similar in composition but different in relative elemental concentrations to those published previously by us for urban airsheds [6]. They are unique to our Cape Grim data and should not be used at other sites. It is not necessary to include a motor vehicle fingerprint for the Cape Grim baseline station because of its isolation from major urban areas as reflected in the very low lead concentrations in Table 1.

Source Apportionment

The identification of these four unique fingerprints given in Table 2 allows us to apply further statistical methods called Chemical Mass Balance (CMB) techniques [11] to determine the absolute and relative contributions of each of these fingerprints to the total measured fine mass. In order to obtain seasonal variations in these fingerprints, monthly averages of the Cape Grim daily data covering the sampling period 1995-98 were used in the US EPA CMB7 calculations [6,7,11]. As expected the seaspray

fingerprint dominated, having a four year average of $(57\pm 9)\%$ of the total PM_{2.5} mass. The monthly variations over this 4 year period are plotted in Fig. 7 and were relative constant as shown by the small standard deviation of only $\pm 9\%$. The amount of seaspray present was strongly dependent on the wind conditions.

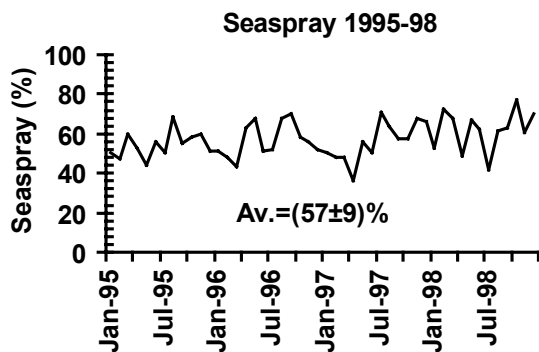


Fig. 7. Percentage contribution of the seaspray fingerprint to the Cape Grim fine mass.

The industry fingerprint which was based on the nss-S and several key trace metallic elements showed quiet distinct seasonal variations, see Fig. 8. Summer contributions peaking at 40% to 50% of the fine mass with winter minima being around 10% to 20% of the total fine mass.

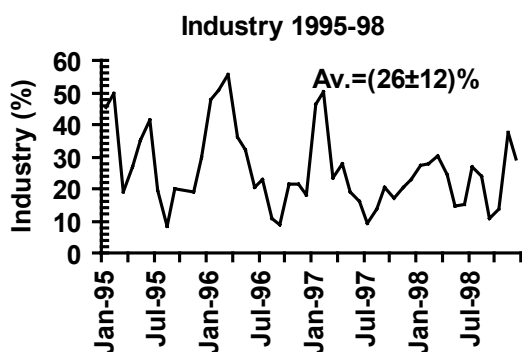


Fig. 9. Percentage contribution of the industry fingerprint to the Cape Grim fine mass.

Contributions from windblown soil averaged only $(2\pm 2)\%$ during the period 1995-98 and were strongly dependent on meteorological conditions. While smoke averaged $(18\pm 9)\%$ of the total fine mass between 1995-98, being higher in the winter months when firewood was burnt for heating.

Conclusions

The ion beam techniques of PIXE, PIGME, PESA and RBS have been used to define twenty different elements present in PM_{2.5} fine particulate matter at global baseline station at Cape Grim, Tasmania. Statistical methods of PCA have been used to define four unique elemental fingerprints that contribute to most of the fine particle mass, namely seaspray,

smoke, soil and industry. These four source fingerprints, which are unique to Cape Grim have then been applied in CMB methods to determine the relative source contributions. The natural components of seaspray and soil generally contributed around 60% to the fine mass with the remaining 40% being anthropogenic and split approximately equally between smoke from biomass burning and wood fires and industrial sources. The anthropogenic component was associated with both local and regional sources some many hundreds of kilometres away on the continental Australian mainland.

Acknowledgments

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