

Fingerprinting and source apportionment of fine particle pollution in Manila by IBA and PMF techniques: A 7-year study

David D. Cohen,^{1*} E. Stelcer,¹ Flora L. Santos,² Michael Prior,¹
Craig Thompson¹ and Preciosa C. B. Pabroa²

X-ray and ion beam analysis (IBA) techniques have been used to characterize fine particle pollution in Manila over a 7-year period. These data have then been used in the latest statistical methods of positive matrix factorization (PMF) to quantitatively identify source fingerprints and their contributions to the total fine particulate mass. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

In recent times, fine particle air pollution (particles with diameters less than 2.5 μm , also known as PM_{2.5}) has been related to adverse health outcomes in USA and Europe, poor visibility in Asia and long range transboundary pollution transport. In 1997 the US EPA introduced a PM_{2.5} standard of 15 $\mu\text{g}/\text{m}^3$ for annual average and 65 $\mu\text{g}/\text{m}^3$ for 24 h maximum. The 24-h goal was reduced further to 35 $\mu\text{g}/\text{m}^3$ in 2006. Several countries in Europe and Asia have followed suit; in Australia, our current PM_{2.5} goals are 8 $\mu\text{g}/\text{m}^3$ for annual average and 25 $\mu\text{g}/\text{m}^3$ for 24 h maximum, much tighter than many other countries. These reasonably tight air pollution goals or standards recognize the deleterious effects of fine particle pollution.

This paper discusses fine particle characterization by ion beam analysis (IBA) techniques and recent developments in their application to source fingerprinting and source apportionment.^[1–9] It provides examples of these applications and their potential through the characterization of a significant PM_{2.5} dataset collected regularly at Manila, Philippines between January 2001 and December 2007. It also shows how wind and back trajectory data can be included to plot fine particle pollution transport and identify possible sources, several thousands of kilometers from the sampling site.

The Techniques and Methods

IBA techniques such as particle induced x-ray emission (PIXE), particle induced gamma ray emission (PIGE), Rutherford backscattering (RBS) and particle elastic scattering analysis (PESA) have been applied for many decades now in the characterization of fine particle pollution.^[3–6,8] These techniques are multielemental, very sensitive, cover the periodic table from H to U, are fast and for the main part nondestructive. They are ideally suited to the analysis of filters containing only a few hundred micrograms of fine particle air pollution. Globally hundreds of thousands of filters have been analyzed using IBA techniques.^[3] In our laboratory alone we have analyzed more than 40 000 fine particle filters during the past 15 years using these four IBA methods on a 2-MV high voltage engineering tandem accelerator. Typically, 2.6-MeV proton beams

of between 10 nA and 100 nA with beam diameters of the order of 8–10 mm have been used to minimize sample damage.

These four IBA techniques have been applied simultaneously to determine the concentrations of the elements H, C, N, O, F, Na, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb on filters in concentrations from tens of percent down to $\mu\text{g}/\text{g}$. Standard He/Ne laser absorption techniques were used to determine the filter black carbon (BC) concentrations^[10] assuming an average fine particle mass absorption coefficient of 7 m²/g. Fine particle elemental concentrations from hundreds of $\mu\text{g}/\text{m}^3$ down to 1 ng/m³ of air sampled are routinely measured by these methods.^[1–5]

The analysis methods are mature and the field has moved onto more sophisticated statistical data interpretation techniques. With the large datasets IBA provides, pollution sources can be statistically fingerprinted and source contributions determined quantitatively.^[3–5,7–9] Older more labor intensive fingerprinting and source apportionment methods, like principal components analysis (PCA) and chemical mass balance (CMB)^[9,11] techniques, are being replaced with positive matrix factorization (PMF) methods.^[7–9,12,13] The PMF technique is a one-step process that quantitatively provides both source fingerprints and daily time series plots for all major source contributions at a given site.^[13]

PMF is a matrix method based on the matrix equation,^[12]

$$\mathbf{X} = \mathbf{F} \times \mathbf{G} + \mathbf{E}, \quad (1)$$

where $\mathbf{X}(n,m)$ is a measurement matrix of n samples (rows) and m chemical species (columns), $\mathbf{F}(p,m)$ is a factor source matrix of p fingerprints (rows) each with m elements (columns), $\mathbf{G}(n,p)$ is a contribution matrix of the p source factors (columns) for each of the

* Correspondence to: David D. Cohen, Australian Nuclear Science and Technology Organization, PMB1, Menai, NSW, 2234, Australia. E-mail: David.Cohen@ansto.gov.au

1 Australian Nuclear Science and Technology Organization, PMB1, Menai, NSW, 2234, Australia

2 Philippines Nuclear Research Institute, 1101 Commonwealth Avenue, Diliman, Quezon City, Manila, Philippines

n samples (rows), and $\mathbf{E}(n,m)$ is an error term, the unexplained part of $\mathbf{X}(n,m)$ which is minimized by the PMF process. The elements of the \mathbf{G} and \mathbf{F} matrices are constrained to be nonnegative values only. The error matrix $\mathbf{E}(n,m)$ is minimized by minimizing Q where,

$$Q = \sum_i \sum_j (e_{ij}/s_{ij})^2, \quad (2)$$

e_{ij} are the elements in the error matrix term \mathbf{E} and s_{ij} are the estimated errors of the experimental measurements. For this work we use,

$$s_{ij} = \text{MDL}_{ij} + \text{SD}_{ij}, \quad (3)$$

where MDL and SD are the minimum detectable limit and experimental standard deviation of element (i,j) of the measurement matrix $\mathbf{X}(n,m)$ respectively. Hence for PMF to work three input matrices are required, the elemental concentration matrix \mathbf{X} , the MDL matrix and the experimental error matrix SD. The standard deviations of the calculated \mathbf{F} and \mathbf{G} matrices are also provided by the codes of Paatero *et al.*,^[13] so the significance of the results can be estimated. These PMF processes and their application have been discussed in detail elsewhere^[13] and only the results will be presented here.

Results and Discussion

The Manila fine particle sampling site was located at Ateneo University, Quezon City, 30 km NE of central Manila at 14° 39'N, 121° 04'E. It was a typical urban Manila site, dominated by traffic, local industry and significant biomass/rubbish burning episodes. Fine particles were collected on 25-mm diameter thin stretched Teflon filters over 24 h every Sunday and Wednesday using an equivalent US IMPROVE cyclone system.^[6] For the PM2.5 cutoff the cyclone system operated at 22 l/min flow rate. Each filter was weighed before and after exposure to $\pm 1 \mu\text{g}$ to determine its gravimetric mass loading.

PM2.5 Data

Over 700 filters were collected between January 2001 and end of December 2007. Figure 1 shows the daily collected PM2.5 mass/ m^3 for this study period.

The large PM2.5 mass peaks, above $100 \mu\text{g}/\text{m}^3$, generally occurred around each Christmas and New Year, showing the effects of fireworks and festive celebrations on air quality in Manila. Apart from these extreme outlier events, there are minor seasonal trends with very little change in the average annual mass of fine particle air pollution over the 7-year study period.

The annual averages ranged from $44.9 \mu\text{g}/\text{m}^3$ in 2001 to $49.6 \mu\text{g}/\text{m}^3$ in 2005 well above the annual US EPA recommended goal ($15 \mu\text{g}/\text{m}^3$) for fine particles. Figure 2 is a histogram of the daily PM2.5 masses shown in Fig. 1. The distribution is not Gaussian but lognormal as expected for this type of environmental data. More than 33% of the time the daily PM2.5 mass exceeded $50 \mu\text{g}/\text{m}^3$ and the US EPA 24 h maximum goal of $35 \mu\text{g}/\text{m}^3$ was exceeded more than 68% of the time during the study period.

Table 1 shows the average PM2.5 fine particle composition obtained from IBA techniques for the 7-year study period. It gives the average, standard deviation, median and maximum concentrations for each of the chemical species measured. Elements Al to Pb were measured using x-ray technique PIXE. Soil estimates were obtained by summing the oxide masses of the five elements Al, Si, Ti, Ca and Fe and organic matter was

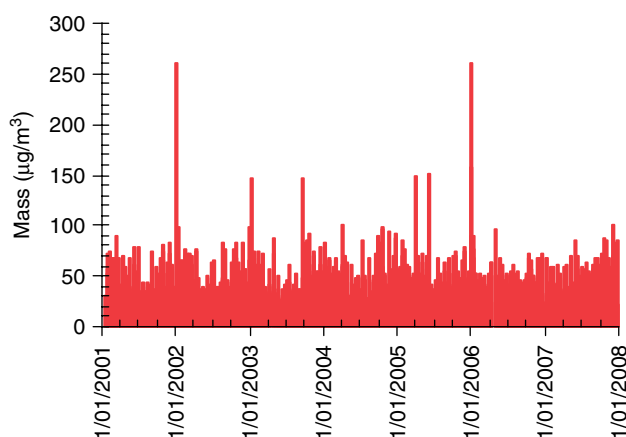


Figure 1. PM2.5 Daily mass measurements for Manila site.

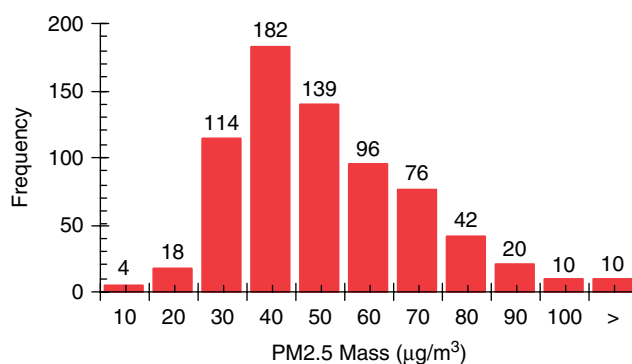


Figure 2. Histogram of PM2.5 daily masses for Manila.

estimated from the PESA (hydrogen) measurement assuming the average organic composition of 9%H, 20%O and 71%C in the standard way.^[2,4] Ammonium sulfate was estimated from the sulfur concentration, assuming a fully neutralized aerosol.^[6]

$K_{\text{non}} = (K - 0.6 \times \text{Fe})$ is the nonsoil potassium, a very strong indicator of biomass burning.^[1,3,5] IBA techniques give the average fine particle composition as 29% BC, 3% soil, 44% organic matter, 16% ammonium sulfate. The average reconstructed mass (RCM), obtained by summing all the analyses and comparing with the gravimetric mass, was $(94 \pm 10)\%$, showing good mass closure for these data.^[5,6] The missing mass was probably nitrates, which were not well held on Teflon filters, and water vapor.^[4,5]

In Manila, the rainy season is generally between May and November with average monthly rainfalls in excess of 400 mm per month for these wetter months, while the monthly rainfall outside this rainy season averages much less than 100 mm. The average monthly PM2.5 mass tended to be $\leq 40 \mu\text{g}/\text{m}^3$ during the rainy season and 20–50% higher in the drier season.

Box and whisker plots for the 7-year study period for percentage soil, ammonium sulfate, BC and organic matter are given in Figs 3–6 respectively. The (+) sign is the monthly mean, the horizontal bar represents the monthly median and the hatched boxes contain 25–75% of data for that month. Outliers are shown as whiskers on the boxes and extreme points as dots for the month.

The soil in Manila was generally much lower (2–5% of PM2.5 mass) than at other sites measured in Australia (5–15% of PM2.5 mass) and this was probably due to the lower average wind speeds

Table 1. Average PM2.5 composition for Manila for the study period

Species	Av.±SD	Median	Max
H (ng/m ³)	2240 ± 1000	2060	8800
Na	110 ± 270	0	2800
Al	62 ± 50	48	400
Si	230 ± 160	194	1100
P	29 ± 19	24	130
S	1700 ± 1100	1500	11 000
Cl	95 ± 210	36	3100
K	390 ± 240	350	3000
Ca	125 ± 95	100	1200
Ti	13 ± 25	10	590
V	17 ± 12	14	64
Cr	1.8 ± 2.1	1.3	15
Mn	10 ± 8	7.6	67
Fe	170 ± 120	140	830
Co	1.3 ± 1.6	0.8	15
Ni	6 ± 5	5.5	44
Cu	10 ± 7	8.1	64
Zn	135 ± 140	96	2000
Br	12 ± 10	10	94
Pb	59 ± 67	40	741
BC (µg/m ³)	13 ± 5	12	33
Soil (µg/m ³)	1.4 ± 0.8	1.2	5.5
Org. matter (µg/m ³)	20 ± 10	18	86
(NH ₄) ₂ SO ₄ (µg/m ³)	7.0 ± 4	6.1	45
K _{non} (ng/m ³)	290 ± 220	250	2900
Salt (ng/m ³)	290 ± 680	0	7100
Mass (µg/m ³)	46 ± 19	42	150

in topical regions as well as the significant rain periods during a year.

Soil and ammonium sulfate showed distinct seasonal trends. Soil was nearly twice as high, in percentage terms, in the drier months, while ammonium sulfate showed the opposite trend being higher in the wetter months. This was not unexpected, as airborne soil was reduced during rain periods. Also ammonium sulfate originates from conversion of SO₂, which, given enough SO₂, proceeds more efficiently in wetter more humid environments.

Monthly distributions of BC and organic matter showed relatively flat percentage contributions to the total PM2.5 mass of 25–35% and 40–50%, respectively.

Clearly there is a chemistry going on as well as chemical composition changes with time. A further, demonstration of the importance of not only using IBA techniques to determine the composition of the aerosol but also of performing quantitative source apportionment to determine the sources of fine particle pollution in these urban type environments.

Traditional fingerprinting and source apportionment

Traditionally researchers have used the two-step techniques of first fingerprinting the sources, usually from source emissions information, and then applying CMB methods^[11] to quantify these fingerprint contributions to the total measured mass. This is a labor-intensive two-step process and requires considerable user input knowledge about the sampling site and what might be contributing to the pollution.

As an example, we calculate the soil fingerprint only from our Manila data for the study period. First we pick the elements Al, Si, Ca, Ti and Fe, which we believe contribute to the soil component of our fingerprint, then we produce the correlation plots of each of these elements with each other. Such a plot is shown in Fig. 7. If indeed each of these elements was uniquely associated with just the soil source, then they would strongly correlate and the gradient of each of the correlation plots can be used to produce the fingerprint for soil^[5] as shown in Fig. 8.

Al and Si have the strongest correlation and were clearly associated with just the one source; however, for the other elements the situation gets more uncertain and the errors in

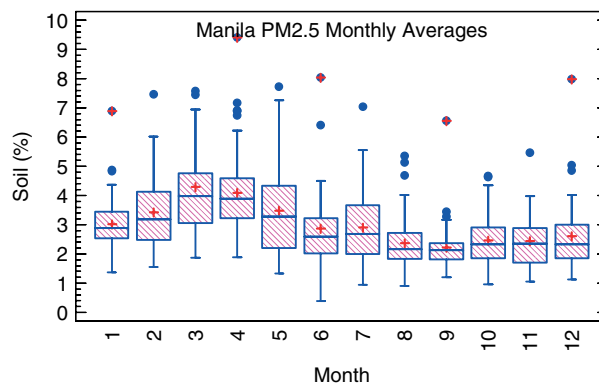


Figure 3. PM2.5 percentage soil in Manila by month.

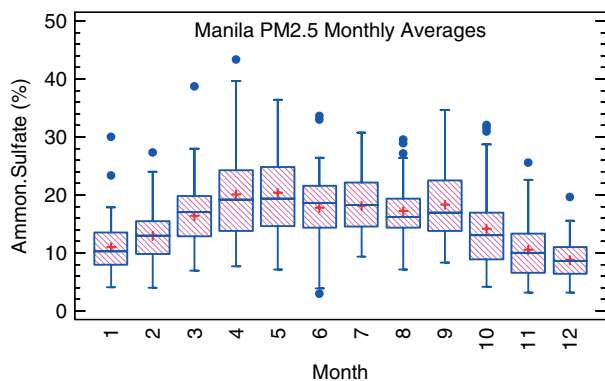


Figure 4. PM2.5 percentage ammonium sulfate in Manila.

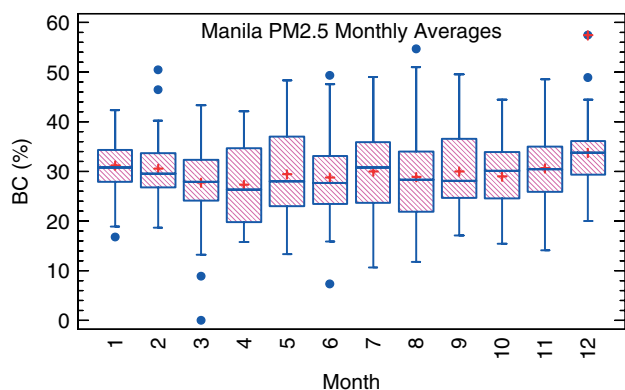


Figure 5. PM2.5 percentage black carbon (BC) in Manila.

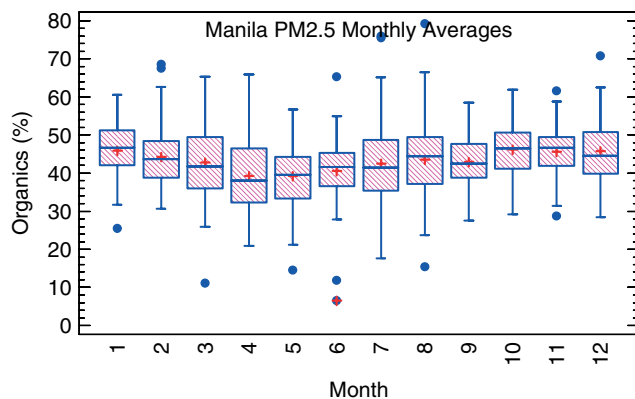


Figure 6. PM2.5 percentage organic matter in Manila.

determining their corresponding relationships were much larger. Oxygen was estimated assuming each of the five elements occurred in its standard oxide form.^[6]

For our Manila data, soil was the easiest fingerprint to extract by this manual technique. Other fingerprints like secondary sulfur, automobiles, smoke and industrial sources proved difficult to extract objectively, because many of these sources contained the same elemental mix in their fingerprints. To assist with this standard, statistical PCA techniques^[12] were used on the entire dataset with extreme and outlier events like the Christmas, New Year, and firework days excluded. Table 2 shows the PCA factor loadings^[12] for five factors accounting for 66% of the variance.

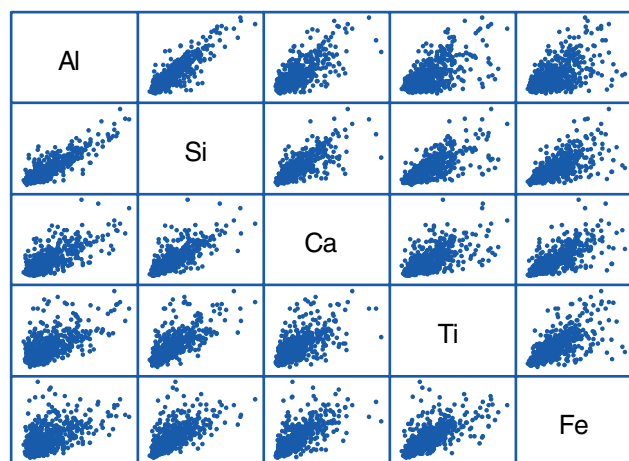


Figure 7. Correlation plots for key soil elements at Manila.

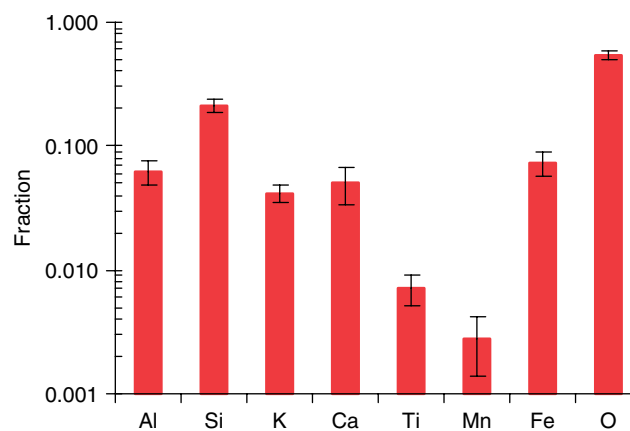


Figure 8. Typical soil fingerprint for Manila PM2.5 particles.

We have named these five factors auto1, soil, auto2/smoke, secondary sulfur and salt as the elements with the highest factor loadings (in any given column) tend to identify these factors as being associated with a source of this type. Again this was a very subjective process and strongly influenced by the user bias and knowledge of the site. The last column in Table 2 is the communality (Comm.), which is the sum of the squared factor loadings across all sources.^[12]

The next step, after using PCA to select the elements in a fingerprint, is just as difficult. As with Fig. 7, one has to use the correlation plots to derive a fingerprint, which can then be used in standard (CMB) codes^[11] to determine the contributions of each of the sources to the total gravimetric mass.

What is needed is a more hands-off approach that takes advantage of the large data set that IBA methods provide when the sampling has been performed over several years.

PMF methods

PMF provides a one-step statistical approach to fingerprinting and source apportionment with significantly less user bias and input than PCA and CMB methods. It is becoming more popular and provides quantitative source fingerprinting and source apportionment.^[7-9]

Table 2. Principal components analysis (PCA) of Manila PM2.5 data set, highlighted loadings are significant

Elt	Auto1	Soil	Smoke/Auto2	2ndryS	Salt	Comm.
Zn	0.839	-0.006	0.213	0.027	0.202	0.791
Mn	0.792	0.115	0.210	0.046	0.298	0.775
Fe	0.725	0.386	0.307	0.093	0.328	0.885
Ni	0.674	0.286	0.027	0.144	-0.186	0.592
V	0.640	0.357	0.128	0.268	-0.366	0.759
Pb	0.485	0.065	0.413	0.078	0.283	0.497
Al	0.044	0.803	0.349	-0.054	0.206	0.814
Si	0.240	0.789	0.271	0.115	0.252	0.830
Ca	0.378	0.698	0.238	-0.010	0.199	0.726
K	0.024	0.470	0.559	0.006	0.305	0.627
Ti	0.085	0.468	0.020	0.016	-0.100	0.237
Cu	0.251	0.027	0.763	-0.051	-0.002	0.648
Br	0.067	0.186	0.722	0.006	0.117	0.574
BC	0.300	0.329	0.668	0.039	-0.166	0.673
H	0.275	0.392	0.632	0.415	-0.063	0.805
P	0.130	0.029	0.078	0.880	-0.039	0.800
S	0.258	0.230	0.181	0.798	0.206	0.831
Cr	0.227	-0.009	0.069	0.214	0.633	0.503
Na	0.034	0.212	0.003	-0.187	0.589	0.428
Cl	0.097	0.237	0.290	-0.531	0.125	0.447

For the Manila data set (with $n = 694$ filters) three matrices were generated, the measurement matrix \mathbf{X} (n, m) with $m = 21$ elements H–Pb and BC, the $\mathbf{MDL}(n, m)$ matrix and the $\mathbf{SD}(n, m)$ matrix. Inputting these three matrices into PMF, selecting the number of factors or fingerprints ($p = 6$) which minimized Q around its expected value of $Q = nm - p(n + m)$, we obtained the fingerprints (\mathbf{F} matrix) shown in Fig. 9 and the daily source contributions for these fingerprints (\mathbf{G} matrix) shown in Fig. 10.

The main user input was in determining the number and names of the six factors, F1–F6. The elements and their fractional contributions associated with each fingerprint, together with the fingerprint contributions to the total fine mass were completely determined statistically by the PMF process. This process also produced output errors for each step as the \mathbf{MDL} and \mathbf{SD} matrices were provided as inputs to the process. Error bars for the fingerprints are shown on plots of Fig. 9. Errors for the source contributions were not shown on Fig. 10 as they would not add to the data presentation but they were typically 5–15%.

Factors 1 and 2, dominated by metals, organics and BC were associated with automobiles. Factor 3 was dominated by K, S, Na and organics and was related to biomass burning and general refuse combustion. Factor 4 had Na and Cl in approximately the correct ratio for sea salt. Factor 5 was dominated by S and H in the ratio consistent with secondary sulfur.

Factor 6 was clearly a soil factor with a range of other metals associated with retrained road dust.

Figure 10 shows the PMF daily percentage contributions to the total fine mass for each of these factors. Note the contributions of the two auto factors, F1 and F2 were summed to produce the auto% data of Fig. 10. The PMF analysis gave the average source contributions for the 7-year study period at the Manila site as, $(69 \pm 13)\%$ autos, $(2 \pm 2)\%$ smoke, $(2 \pm 5)\%$ sea, $(22 \pm 13)\%$ secondary sulfur and $(4 \pm 3)\%$ soil. Again we see similar seasonal variations in the secondary sulfur and soil fingerprints as discussed earlier in Figs 3–6. Figure 10 also shows that the percentage of sea

salt at the Manila site tended to be high when the secondary sulfur was lowest, in the driest November–January period each year.

Figure 11 shows the sum of the individual PMF fingerprint mass contributions compared with the gravimetric mass for every sampling day of the study period. The agreement was excellent over the mass range from $10 \mu\text{g}/\text{m}^3$ to $100 \mu\text{g}/\text{m}^3$.

Figure 12 is a comparison of the daily soil source estimates at Manila for the manually generated soil fingerprint, generated in Fig. 8 and the PMF soil fingerprint of Fig. 9. Clearly all major trends were predicted and the correlation was excellent. The manually generated fingerprint generally under estimates the PMF one because it only contains 5 elements while the PMF fingerprint contains 14 of the 21 measured elements.

Back trajectory techniques

Having determined the sources and their contributions to the fine particle mass at the site, we turn to Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) back trajectory techniques to trace possible medium and long range transport of pollution to the measurement site. HYSPPLIT and its use have been described elsewhere.^[14] It is based on global synoptic weather patterns using a $1^\circ \times 1^\circ$ grid spacing across the area of interest. It uses up to 10-day back trajectories for every hour of every day for sites in both the northern and southern hemisphere and is readily available on the web.^[14]

Close inspection of secondary sulfur source (F5) of Fig. 10 shows two distinct peaks, separated by a clear minimum in 2006. These peaks occurred on the 28–31 May and 13–17 September 2006. Figure 13 is a plot of 5-day back trajectories, every 12 h for these two distant periods in 2006. Two starting heights of 300 and 500 m have been selected to span the heights of possible inversion layers over the sampling site at Manila. These two heights provide similar back trajectories for trajectories in the same time periods, providing consistent evidence for the possible origins of the air

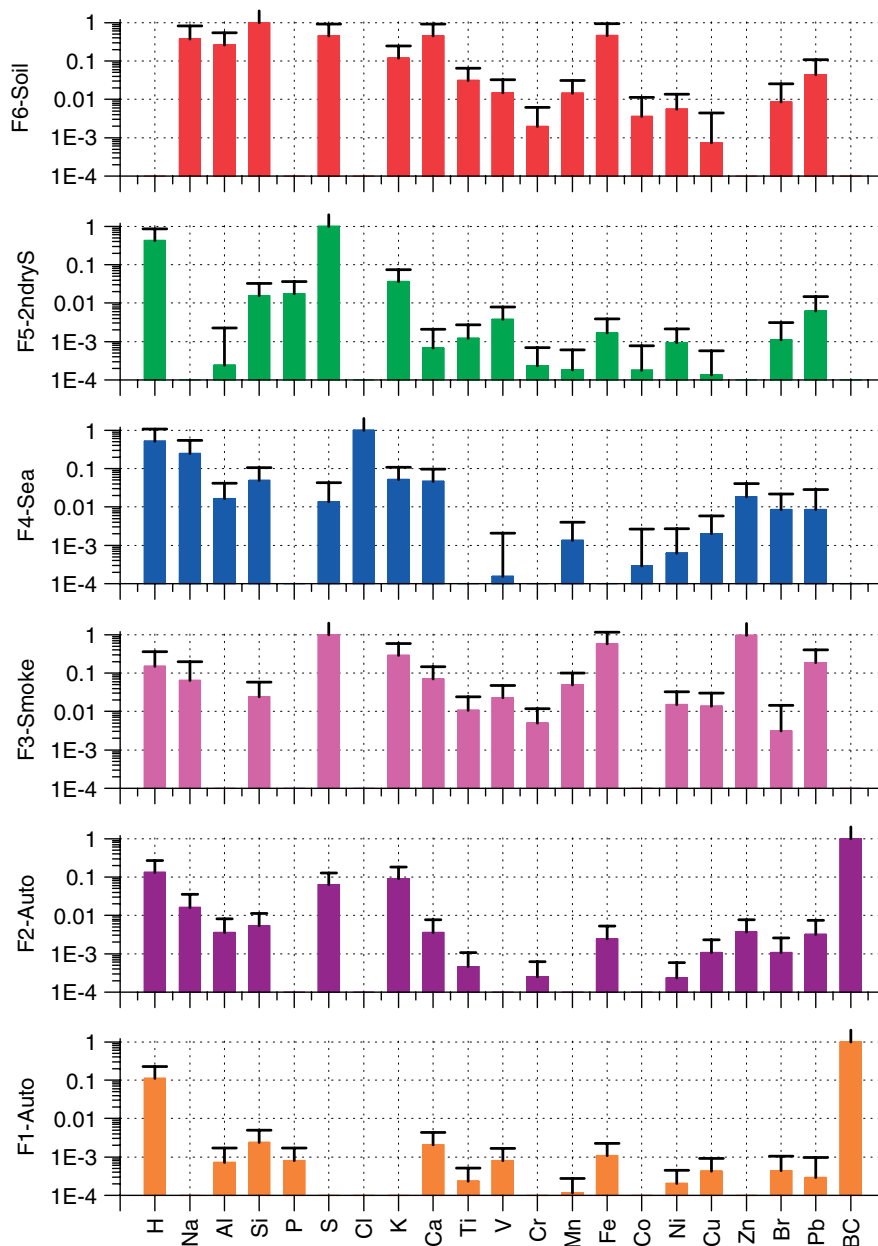


Figure 9. PMF source fingerprints for Manila, 6 factors.

parcels reaching this sampling site during these two separate sampling times.

The figure clearly shows that for May 28–31 peak the secondary sulfur source originated from the west of the Manila site, with the general ‘fetch area’ for the 5 days extending over the South China Sea to the coast of Vietnam and then turning north through Hong Kong to the industrialized regions of eastern China. For the 13–17 September period the general ‘fetch area’ was east of Manila passing over several local islands before extending out over clear ocean, suggesting that a more local secondary sulfur source contributed during this period.

This is just one example of how HYSPLIT might be used to determine general ‘fetch areas’ associated with local or transboundary transport or pollution transported at certain times or seasons. Clearly, it can also be used to look at possible sources

of pollution associated with individual outlier days or extreme events that may occur during a study period.

Summary

We have clearly demonstrated that PMF techniques can statistically produce quantitative and meaningful fingerprints as well as their contributions, provided the data set is large enough. X-ray and IBA techniques provided information on over 20 chemical species and are rapid enough to analyze hundreds of samples in a short time. A hundred filters or more are generally sufficient to perform a meaningful PMF analysis. If even more data is available, then these techniques are excellent. We have found that PMF techniques typically produce one to two more factors or fingerprints per given data set than standard PCA techniques. The PMF technique was significantly superior to previous PCA and CMB methods, as it

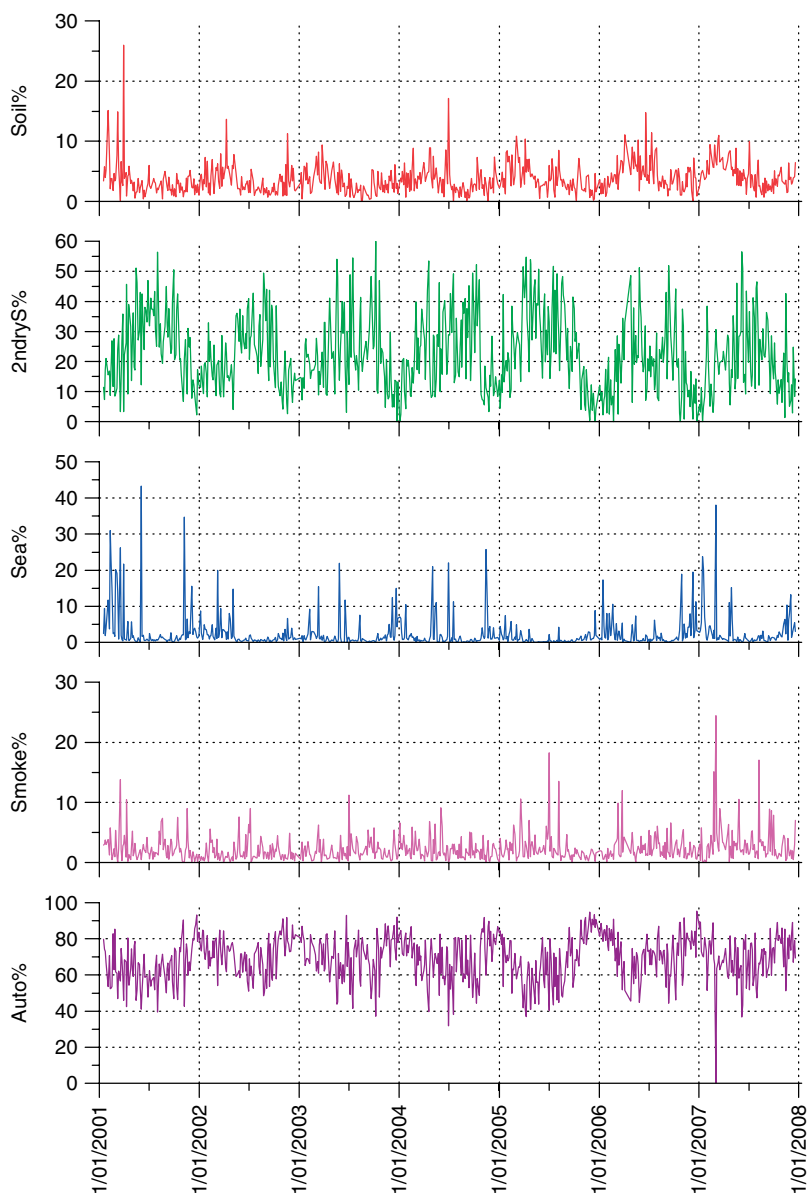


Figure 10. PMF daily source contributions for the sources identified in Fig. 9.

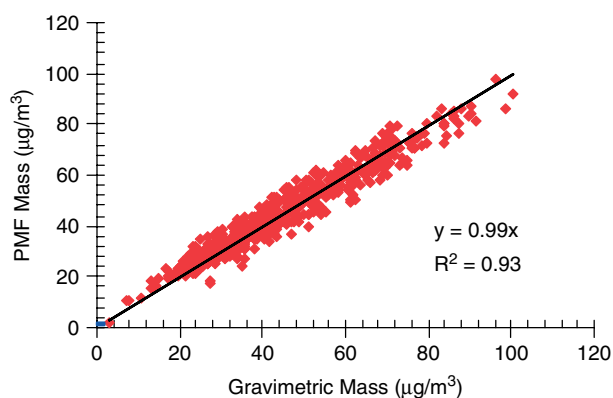


Figure 11. Plot of PMF mass against gravimetric mass for PM2.5 Manila dataset.

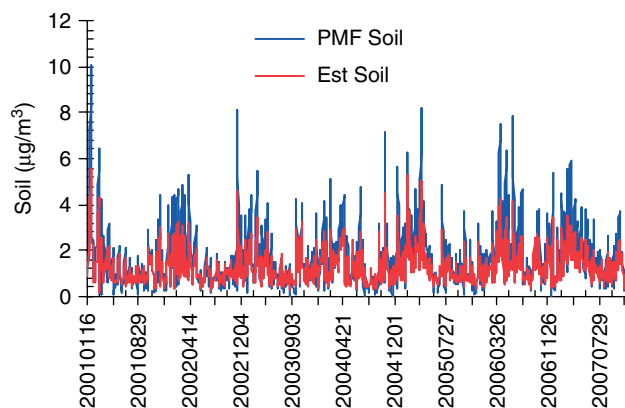


Figure 12. Comparison of PMF source contributions with soil estimates form using the five key elements for soil from Malm *et al.*^[6].

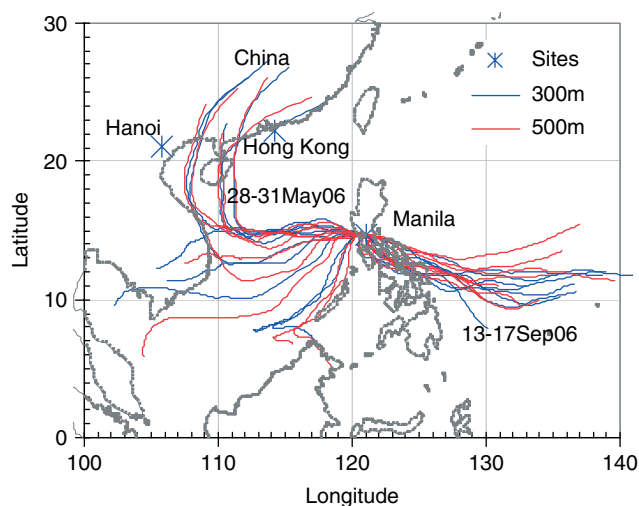


Figure 13. HYSPLIT 12 hourly, 5 day back trajectories for 300 and 500 m heights for high secondary sulfur (F5) events between May 28–31, 2006 (west) and September 13–17, 2006 (east) at Manila.

is purely a statistical approach, is a one-step method, and requires minimal user interpretive input. These IBA and PMF techniques have been successfully applied to a unique 7-year fine particle data set, to determine both the daily composition and the daily source contributions at the Manila sampling site. This will greatly assist in the understanding and management of air pollution in these types of urban environments.

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