Characterisation of PM2.5 and PM10 Fine Particle Pollution in Several Asian Regions

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Abstract

PM2.5 and PM10 aerosol size fractions have been measured every Wednesday and Sunday for a 24 hour period at Manila in the Philippines, Hong Kong, Cheju Island in South Korea, Hanoi in Vietnam and Sado Island off the west coast of Japan. Accelerator based ion beam analysis (IBA) techniques have been used to quantify major components as well as significant trace elements. These included, total hydrogen, elemental carbon, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, Vi, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, and Pb with sensitivities close to or below 1ng/m^3. All sites except the Sado Island site in Japan had annual average PM2.5 concentrations well above the US EPA goal of 15 µg/m^3. [PM10/PM2.5] ratios were typically (2.2±0.4) averaged across all sites for the whole year.

Keywords: PM2.5, PM10, aerosols, fine particle characterisation, Asian region, IBA techniques.

1. Introduction

The uncertainty in fine particle aerosols concentrations and chemistry significantly limits our ability to assess the effect of natural and human induced changes on global climate forcing (IPPC 1995) and human health (Dockery1993). Since the beginning of 2001 we have been regularly monitoring both fine (PM2.5) and coarse (2.5µm to 10µm) size fractions in collaboration with researchers from Australia, Hong Kong, Korea, Philippines, Vietnam and Japan as part of a five year Aerosol Characterisation Experiment in Asia called ACE Asia (Arimoto et al 1999). Accelerator based ion beam analysis (IBA) techniques, described previously, (Cohen et al 1996, 1998, 1998b, 1999, 2000) have been used to quantify and characterise aerosols collected on filters at sites in these five Asian countries during 2001.

2. Sampling and Sites

Two different types of sampling unit were used in this study, the ASP PM2.5 fine sampler (Cohen et al 1996), based on the US IMPROVE cyclone system (Malm et al 1994) and the GENT stacked filter unit (SFU) with a coarse (2.5µm to 10µm) and a fine (less than 2.5µm) 47 mm Nuclepore filter (Hopke et al 1999 and Maenhaut et al 1993). The ASP sampler used a 25 stretched Teflon filter and had a flow rate of 22 l/min, the GENT sampler used a flow rate of 16 l/min.

The ASP samplers were use to fully characterise the fine fraction (PM2.5) as collection on Teflon substrate allowed for excellent ‘mass closure’ (Cohen et al 1996,1998b, 2000). Data from the GENT sampler primarily provided [PM10/PM2.5] ratios for the total masses and elemental and chemical species measured. PM10 concentrations were obtained by the addition of the fine (PM2.5) and the coarse (2.5µm to 10µm) fractions.

Sampling occurred at the following five sites in Asia during 2001.

a) Manila, Philippines, ASP (ASP59) and GENT (GAS62) samplers located 13 km NE of central Manila at 14°39’N 121°03’E. For this study sampling commenced on 16 January 2001.

b) Hong Kong Island, ASP (ASP60) and GENT (GAS61) samplers located on the SE corner of Hong

Kong Island at Cape D'Aguilar, 22°12'N 114°15'E, 60 m above sea level on a cliff facing the South China Sea. The population density on the Cape is relatively low and the closest industrial town is Chai Wan 10 km to the NW. Prevailing winds for this site are E-SE in the summer (June to August) and N-NE in the winter (December to February) bringing pollution from the Chinese mainland. For this study sampling commenced on 3 January 2001.

c) Cheju Island, South Korea, ASP (ASP63) and GENT (GAS64) samplers located on the western coast of the Island at 33°18'N 126°09'E, facing the Chinese mainland across the Yellow Sea. The island is approximately 480 km south of Seoul. For this study sampling commenced on 30 March 2001.

d) Hanoi, Vietnam, ASP (ASP65) sampler only located outside Hanoi at 21°01'N 105°51'E, 100 km west of the South China Sea and NE of central Hanoi in an urban/ industrial area. A GENT sampler data was not reported here as similar data for Vietnam has been reported previously by Hien et al 2002. For this study sampling commenced on 25 April 2001.

e) Sado Island, Japan, ASP (ASP66) and GENT (GAS67) samplers located on the north western coast of the Island off the western coast of central Japan at 38°12'N 138°21'E, atop a 90 m cliff facing the Korean mainland across the Sea of Japan. The island is approximately 304 km NW of Tokyo. For this study sampling commenced somewhat later than the other sites on 16 September 2001.

These five sites within east and south east Asia cover a triangular area bordered by Hanoi, Sado and Manila of approximately 2.8Mkm^2.

Where possible samples were generally collected over a 24 hour period from midnight to midnight every Wednesday and Sunday throughout the year. For some sites during heavily polluted periods samplers were operated on a two hours on two hours off basis over the 24 hour collection period to avoid reduced flow rate and filter clogging problems.

3. Results and Discussion

The Teflon and Nuclepore filters collected were posted to Australia for analysis at ANSTO. During the twelve month sampling period 249, 327, 237, 68 and 91 filters were analysed from the Manila, Hong Kong , Cheju Island, Hanoi and Sado Island sites respectively. Each filter was weighed to ±2µg before and after exposure to determine the total particulate mass deposited. Standard He/Ne laser (wavelength 633nm) absorption techniques were used (Cohen et al 2000) to measure the elemental carbon concentration, assuming a mass absorption coefficient of 7 m^2/g.

IBA techniques (Cohen et al 1996,1998) were used to determine H, C, N, O, F, Na, Al, Si, P, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb at concentrations with sensitivities close to or below 1ng/m^3. The measurement of so many different elemental species allowed estimates of the significant aerosol components to be made in the standard way (Malm et al 1994). For example, soil was estimate from the five key elements Al, Si, Ca, Ti and Fe assuming they occurred in their oxide states, ammonium sulfate from sulfur assuming the sulfate ion was fully neutralised, seasalt from Na and Cl concentrations and organic matter from the hydrogen, not associated with ammonium sulfate, assuming an average organic matter composition of 9%H, 20%O and 71%C. These five major components generally accounted for 70% to 95% of the fine (PM2.5) gravimetric mass.

3.1. PM2.5 Data

The 24 hour average daily mass concentrations for each of the five sites during the sampling period are shown in Fig. 1. Each of the graphs has the same vertical mass scale except for the Sado Island site which was a more remote site and experienced lower mass concentrations. The US EPA PM2.5 goal is 15 µg/m^3 for the annual average and 65 µg/m^3 for 24 hour maximum. All sites, except the Sado site exceeded both these goals. At each site the daily variations were large and varied by a factor of 5 or more.

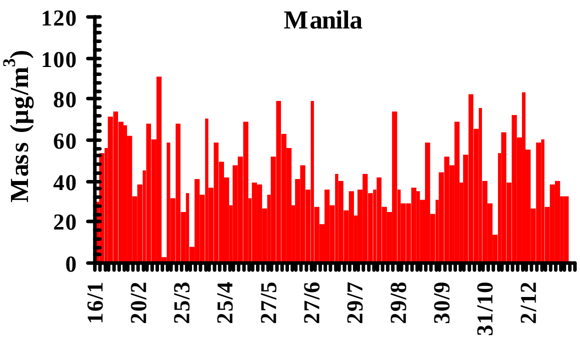

Fig. 1a.

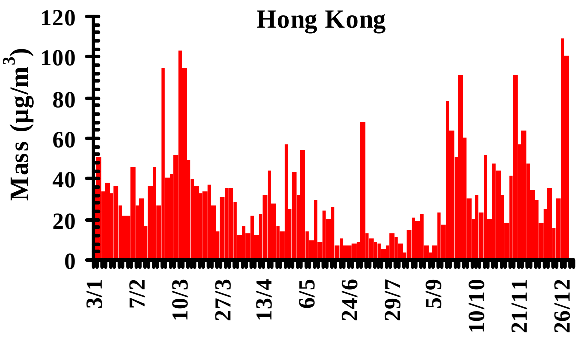

Fig. 1b.

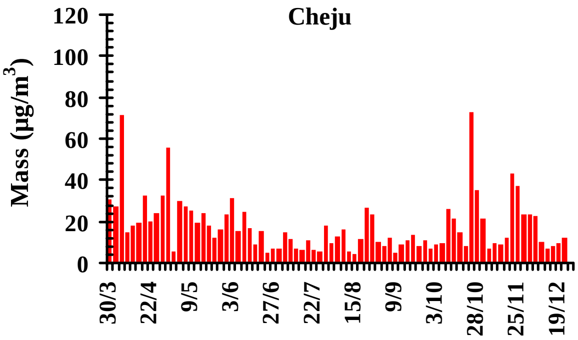

Fig. 1c.

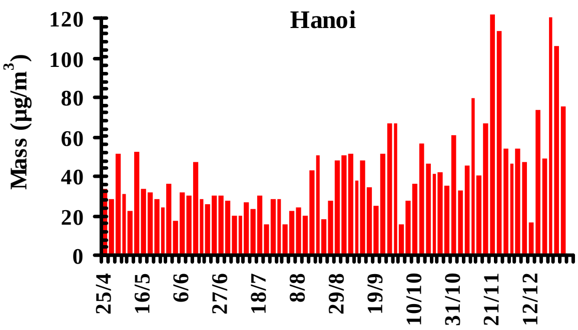

Fig. 1d.

PM2.5	Manila	Hong Kong	Cheju Island	Hanoi	Sado
EltC (%)	28±11	7.0±5	8.3±7	8.1±3	8.8±4
Soil (%)	2.74±2	7.5±9	10.4±18	10.5±9	5.36±5
Amm. Sulfate (%)	16±8	40±26	43±25	25±12	39±28
Organics (%)	45±22	19±24	11±17	25±14	7.9±14
Seaspray (%)	3.39±3	9.5±7	8.3±6	2.44±2	14±10
Trace Elt (%)	0.63±0.3	0.79±0.3	0.46±0.2	1.65±2	0.39±0.1
Non Soil K (%)	0.46±0.4	1.41±1.5	0.86±1.0	1.24±0.6	0.92±0.9
Sum (%)	96±47	85±72	82±77	74±42	77±62
Av. Mass (µg/m^3)	45±18	31±22	18±13	42±26	8.9±6
Max. Mass (µg/m^3)	90	109	73	155	23
Cl loss (%)	83±29	89±19	96±11	83±18	65±36

Table 1. The annual average concentrations of the major aerosol components for the fine fraction for each site.

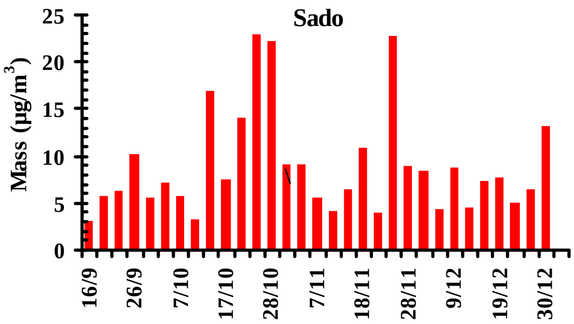

Fig. 1e. PM2.5 daily fine particle mass (µg/m^3) for the Manila (a), Hong Kong (b), Cheju Island (c), Hanoi (d) and Sado Island (e) sampling sites for 2001.

Seasonal variations of a factor of 2 to 5 are also obvious, particularly in the longer term records at the Manila, Hong Kong and Cheju Island sites. Hien et al 2002 report annual PM2.5 values between 33 µg/m^3 and 36 µg/m^3 for the past three years at Hanoi totally consistent with the data of Fig. 1d.

Table 1 shows the annual average concentrations of the major aerosol components for the fine fraction for each site. The sum of all measured components lies between 74% and 96% of the measured gravimetric mass. Demonstrating the good mass closure obtained for this data.

The 4% to 26% missing mass was mainly water vapour and nitrates. The IBA measurements were performed in vacuum, hence all water vapour was lost using analysis and nitrates were not measured and are not well held on Teflon filters. The errors quoted are the standard deviations for the sampling period. These were large because of the large daily variations as demonstrated by the plots of Fig.1. Measurement errors were much smaller typically ±5% to ±15%. Trace elements were calculated from the sum of P, V, Cr, Mn, Co, Ni, Cu, Zn, Br and Pb. Non soil K was an estimate of potassium associated with smoke and biomass burning. The urban site of Manila had the highest organic matter and elemental carbon but the lowest smoke (non soil K) probably associated with the combustion of organic material not related to vegetation burning. The percentage of Cl loss was calculated by subtracting the Cl associated with seasalt from the total measured Cl. Chlorine has several sources besides seasalt (automobiles, industry etc). The fact that the Cl loss, in the fine fraction, was large at all sites can be explained by the relatively high percentage of sulfate present at all sites. Cl loss correlates well with high sulfate concentrations. The 65%-96% Cl loss in the PM2.5 fraction reported here was significantly higher than the 15%-16% reported by Cheng et al 2000 for PM10 at the same site.

Soil is a key component in aerosols in the Asian region (Arimoto et al 1999). In particular fine soils can be transported many hundreds if not thousands of kilometres from their source. North western China and the Gobi Desert region are known sources of 'yellow dust' across our sampling region at particular times of the year. If the soil component measured at each of our five sites originated from a similar source then we would expect it to have similar elemental characteristics.

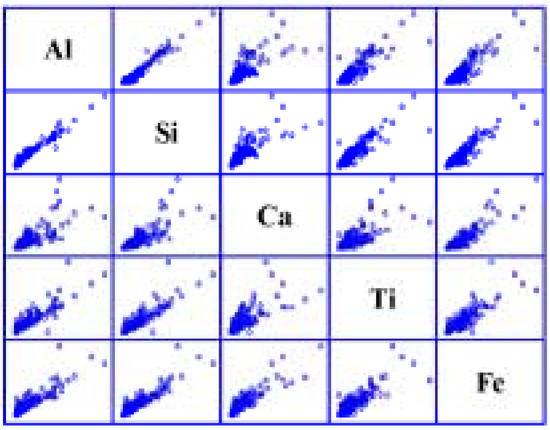

Fig. 2. Correlation plot for the five major soil components for all sites for PM2.5 data taken during 2001.

Fig. 2 is a correlation plot for the five major soil components used here for all sites during the sampling period 2001. It shows remarkably consistent correlations for all elements across all five sites. Suggesting a similar and common soil component for the region. Elements associated with Ca have the largest spread suggesting that at least one of the sites has more than one source of Ca (cement production or construction activities maybe). Temporal variations of the PM2.5 soil component show similar correlations between sites as demonstrated by the monthly average box and whisker plots of Fig. 3 for the Hong Kong and Cheju Island sites, for example. The box encloses the middle 50%, the horizontal line in the box represents the median. Each whisker is drawn from the 1st and 3rd quartile to the smallest or largest point 1.5 interquartile ranges from the box. Outliers outside the whiskers are plotted separately as filled circles. The + symbol inside the box represents the mean.

The Hong Kong and Cheju Island sites are some 1,800 km apart, but both showed significant increases in soil in the months of April, September and October. In particular, the 7 to 18 April 2001 was an exceptional period at both these sites. On 13 April the PM2.5 masses were 32µg/m^3 and 71µg/m^3 and the soils were 10.2µg/m^3 and 22.3µg/m^3 at the Hong Kong and Cheju Island sites respectively. That is, the soil fraction of the fine component at both these sites was 32% of the total fine mass on this day, far in excess of the mean values quoted in Table 1.

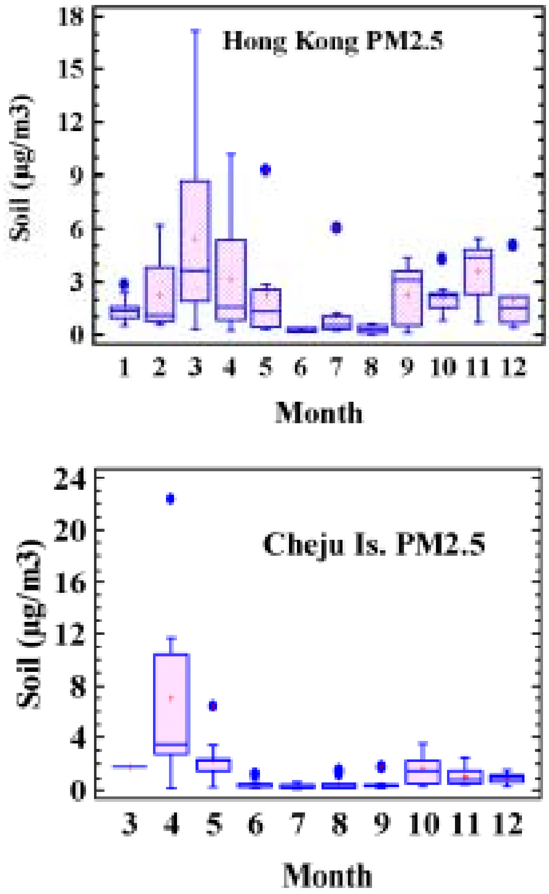

Fig. 3. Box and whisker plots for monthly average PM2.5 soil at Hong Kong and Cheju Island sites for 2001.

Fig. 4. is a five day back trajectory plot from the NOAA Air Resources Laboratory for the Hong Kong site for three heights 100m, 200m and 500m above sea level for 12 April 2001 showing clearly that dust from the central and western regions of China would impact on the Hong Kong site after only a couple of days.

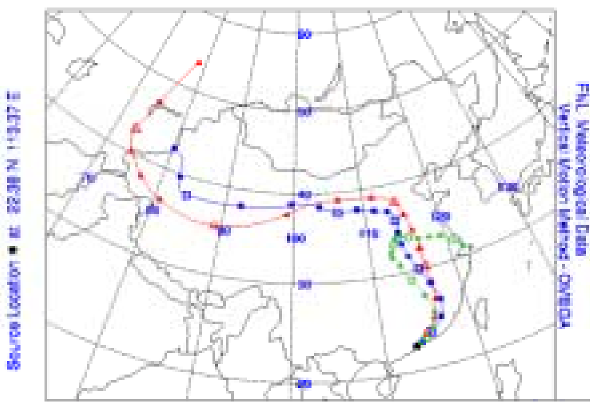

Fig. 4 NOAA Air Resources 5 day back trajectory plot from Hong Kong for 12 April 2001, triangles 100m, squares 200m and circles 500m above seas level.

This could only happen with fine particles, large or coarse particles would not be transported over these large distances.

Ammonium sulfate was the major component at all of the sites except Manila. In the fine fraction it is typically anthropogenic and has several sources including automobiles, coal and oil combustion and industry. It was estimated from the total sulfur concentration assuming the sulfate ion was fully neutralised. This assumption does not hold at all sites at all times, as suggested by the large chlorine loss which requires significant acidic aerosols as discussed earlier. The Hong site had one of the consistently largest average percentage sulfate concentrations (40±26)% with a PM2.5 total mass of (31±22) μg/m^3. Fig. 5 is a box and whisker plot for the average monthly ammonium sulfate concentration at Hong Kong during the study period.

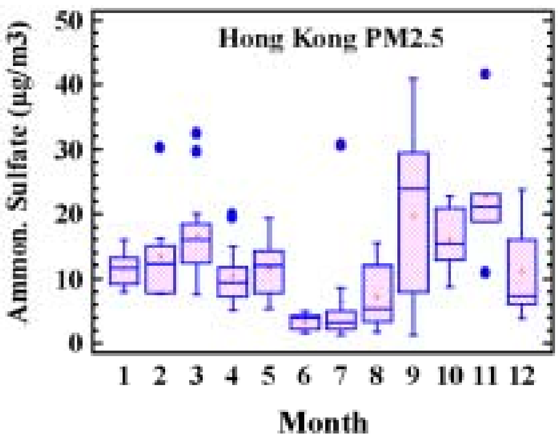

Fig. 5. Box and whisker plots for monthly average PM2.5 ammonium sulfate at Hong Kong for 2001.

It shows strong seasonal variations having maximum concentrations with large excursions in the winter periods and minimal concentrations in the summer.

Elemental carbon is a key component of many combustion products such as coal, oil and vegetable matter. For sulfur containing products such as coal or oil we would expect elemental carbon to correlate with sulfur. Fig. 7 is a plot of elemental carbon against sulfur for all sites during the study period. There are two distinct data groups, those with elemental carbon associated with sulfur and those with excess elemental carbon not associated with sulfur. For the first group the correlation is good with EltC =(0.695±0.024)*S and a correlation coefficient of R^2=0.78. The bulk of the points with large elemental carbon (EltC > 6 μg/m^3) and low sulfur originated from the Manila data, demonstrating that elemental carbon in Manila is not dominated by coal or oil combustion products.

Fine K is a recognised tracer for biomass mass burning (Cohen et al 1996, Malm et al 1994). Fig. 8 is a plot of fine potassium against elemental carbon for all sites. Again there are two distinct groups of data, namely, elemental carbon associated with vegetation burning with EltC=(887±66)+(2.39±0.11)*K with R^2=0.66 and, excess elemental carbon not associated with fine K.

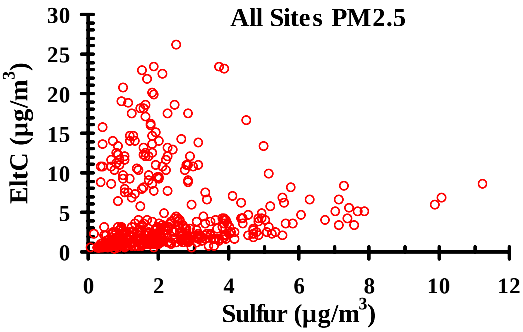

Fig. 7. A plot of elemental carbon against sulfur for all sites during the study period.

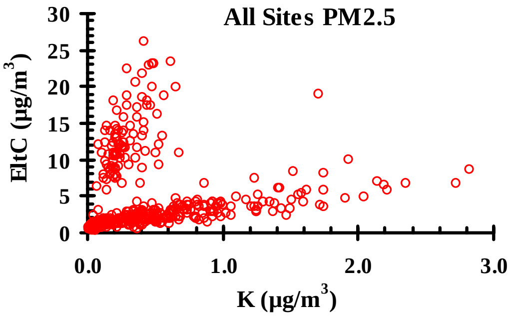

Fig. 8. A plot of fine potassium against elemental carbon for all sites.

Again the second group with high elemental carbon above 6 μg/m^3 was associated mainly with data from Manila site, demonstrating that the elemental carbon at Manila was not dominated by smoke from vegetation burning.

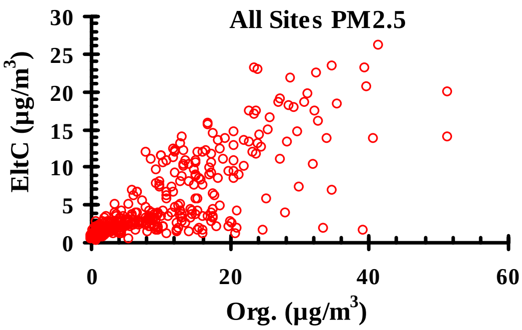

Fig. 9. A plot of fine organic matter against elemental carbon for all sites.

Fig. 9 shows a similar plot of elemental carbon against estimated organic matter. Again there are the two distinct groups, high elemental carbon associated with medium to high organic matter and low elemental carbon associated with low to medium organic matter. The first group is again associated with data from the Manila site and, unlike all other sites, elemental carbon and organic matter in this group were strongly correlated. This group represents sources of combustion of C, H, and O containing compounds. For Manila alone EltC=(0.549±0.018)*Org with an R^2=0.92.

3.2. PM10 Data

Data from the GENT samplers at all sites except Hanoi were used to determine the [PM10/PM2.5] size fraction ratios for the total mass as well as each measured elemental species. The PM10 fraction is obtained by summing the coarse and fine fractions as measured by the GENT samplers. Fig. 10 is a plot of PM2.5 against PM10 mass fractions for all sites for the study period.

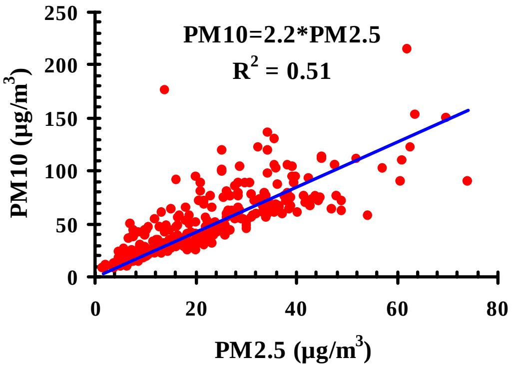

Fig. 10. GENT sampler PM10 versus PM2.5 data

The correlation is good with the average ratio being [PM10/PM2.5]=(2.2±0.4), demonstrating that on average the fine fraction is about 45% of the PM10 fraction. The high points above the line of best fit with high PM10 values were days associated with the extreme soil events at Hong Kong and Cheju Island in April 2001 previously discussed. As expected these showed a higher coarse fraction.

4. Summary

The average PM2.5 aerosol size fractions for five Asian sites have been measured and found at four of the sites to exceed the current US EPA annual and daily goals. Up to 25 different chemical and elemental species have been measured with sensitivities down to 1ng/m^3. Five major components of elemental carbon, ammonium sulfate, soil, organic matter and seaspray were found to account for more than 70% of the total fine particle mass. The [PM10/PM2.5] ratios were very consistent across all sites and seasons being around (2.2±0.4) demonstrating that on average the fine fraction is about 45% of the PM10 fraction.

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