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Fine particle characterisation, source apportionment and longrange dust transport into the Sydney Basin: a long term study between 1998 and 2009

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ABSTRACT

Ion beam analysis techniques have been used to characterise fine particle (PM_{2.5}) pollution in the Sydney Basin between 1 July 1998 and 31 December 2009. Nearly 1 200 filters were obtained and analysed for more than 21 different chemical species from hydrogen to lead. Positive matrix factorisation was then applied to this significant database to determine 7 different source fingerprints and their contributions to the total PM_{2.5} mass. Most of these sources originated in the Sydney Basin, however there were significant windblown soil sources that originated not just from desert regions in central Australia but also from large agricultural regions around 500 km south west of the Basin. This long range transport of fine dust was tracked using hourly back trajectories for every sampling day during the study period and showed that 33% of extreme dust events were probably originating from agricultural regions and not the central desert regions of Australia as first thought.

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1. Introduction

Australian Nuclear Science and Technology Organisation (ANSTO) has been applying accelerator based Ion Beam Analysis (IBA) methods to the characterisation, source quantification and identification of long-range transport of fine (PM_{2.5}) airborne particulate matter for many years (Cohen et al., 1996; Cohen, 1998; Cohen et al., 2004a; Cohen et al., 2004b; Cohen et al., 2009; Cohen et al., 2010). Here we report on a long term (1998–2009) study at an urban site, Liverpool, within the greater Sydney Basin. In particular we look at two aspects, firstly the total fine mass, its chemical composition and possible sources and secondly we identify significant dust storm events during the 11 year study period. For the first time, we report quantitatively on the possible origins of these dust events which impact on the Sydney Basin.

The Sydney Basin (dotted kidney shaped line shown in Figure 1) is centred on the largest city in Australia, it fronts the eastern seaboard of Australia and is bounded in the west by the Great Dividing Range which runs parallel to the eastern coast of Australia defining the western edge of the Basin as shown in Figure 1. The Basin is about 200 km long and 100 km wide, over 4.5 million people inhabit the Basin along with nearly 3 million motor vehicles which travel an average of 15 000 km/year. This Basin is a natural trap for fine particle pollution generated locally. In the winter months there are significant inversions which hold and concentrate pollution in the Basin. In the summer there are significant sea

breeze effects which sweep pollution inland from the coast and northwards up along the western edge of the Basin.

There are also pollution sources external to the Basin that enter under favourable meteorological conditions and then circulate within the Basin for several days before major synoptic weather patterns move them on. Windblown soil and desert dust are such external sources (Leslie and Speer, 2006). Australia is one of the driest continents on earth. There are around a dozen different desert regions, lying mainly in the central and north western parts of the country. These deserts cover around 18% of the total continental land mass. The rainfall in these desert and semi-arid regions can be as little as 100-200 mm/year and with the summer temperatures exceeding 40 $^{\circ}\mathrm{C}$ for long periods of time the evaporation rates are very high. As a consequence of these conditions Australians are accustomed to experiencing between 5 and 10 significant dust storm events each year when the meteorological conditions are favourable for their production (McTainsh et al., 2005; McGowan and Clark, 2008). Some of these dust storms impact major population areas. Again, depending on the local meteorological conditions they can be considered as local dust storms or, in the case of the larger ones, may result in longrange dust transport (Qin and Mitchell, 2009). In the larger dust storms, soil can be transported from desert regions across major cities reducing visibility to less than 1 km for many hours and many millions of tonnes of valuable top soil can be transported hundreds and even thousands of kilometres from their source regions (Ekstrom et al., 2004). Also an increase of aerosol loading has been observed in some areas following the onset of severe drought conditions in 2002 (Mitchell et al., 2010).

In this long term study covering the period from 1998–2009, unlike other studies in the Sydney Basin, we quantify and characterise fine particulate matter into possible source fingerprints. We then focus on fine soil or dust events as measured at the inner Sydney urban site of Liverpool, and identify their possible source regions hundreds of kilometres outside the greater metropolitan region.

2. The Sampler and Its Location

The Liverpool sampling site was located at latitude -33.925° and longitude 150.925° some 20 km west south west of Sydney in the southern part of the Sydney basin [see the (*) in Figure 1]. It is a typical urban site surrounded by 2–3 bedroom dwellings and several light industrial areas within a 20 km radius.

Sydney has four distinct seasons, summer (December to February), autumn (March to May), winter (June to August), spring (September to November). Summer daytime maximum temperatures average around 26 °C but typically there are about 14 days in summer with daily maxima over 30 °C. This, together with the long hours of sunlight, is ideal for the conversion of SO_2 gas emitted from power generation and industry to secondary sulphate particles. The winters are mild with maximum daytime temperatures around 16 °C with occasional morning frosts inland from the coast. Sydneysiders often burn significant amounts of wood for heating during winter, especially those living away from the coast. This can produce significant smoke in the winter when calm conditions and inversion layers tend to trap this type of pollution.

Samples were collected between 1 July 1998 and 31 December 2009 every Sunday and Wednesday from midnight to

midnight using an IMPROVE cyclone system with a $PM_{2.5}$ cut off for flow rates of 22 L/min. The filter was a 25 mm diameter stretched Teflon being about 250 $\mu g/cm^2$ thick before exposure. Nearly 1 200 filters were collected during the study period.

3. Fine Particle Characterisation

Each Teflon filter was weighed before and after exposure. Standard He/Ne laser transmission techniques were used to estimate the total black carbon (BC) content for each filter (Taha et al., 2007) using a mass attenuation coefficient, ε =7 m²/g. Four simultaneous IBA techniques were used to determine 21 different elemental concentrations from hydrogen to lead for concentrations down to 1 ng/m³ of air sampled. These have been described in detail previously as well as their associated error estimates (Cohen et al., 1996; Cohen, 1998; Cohen et al., 2002; Cohen et al., 2004a; Cohen et al., 2004b) and will not be reproduced here.

The average, median, standard deviation and maximum values obtained at the Liverpool site for the study period are given in Table 1 for the 20 different elemental species measured, BC and the PM_{2.5} gravimetric mass together with estimates of fine soil, sea salt, ammonium sulphate, non-sea salt sulphur (nssS) and organics obtained in the standard way described previously (Malm et al., 1994; Cohen et al., 2010). The reconstructed mass (RCM) was obtained again using the definitions of Malm et al. (1994) and represents the best estimate of the sum of all the measured quantities and can be compared directly with the gravimetric mass to produce a mass closure estimate for this data set of (82±12)% of the gravimetric mass. This is considered good mass closure for datasets of this type and provides excellent confidence for the source apportionment estimates discussed later. The missing 18% of mass was probably nitrates and water vapour (Cohen et al., 1998).



Figure 1. Sydney Basin (dotted kidney shape) on the Australian east coast. The sampling site at Liverpool (*) is about 20 km west south west of downtown Sydney.

Table 1. Typical average, median, standard deviation and maximum $PM_{2.5}$ concentrations for all 1 170 sampling days between 1 July 1998 and 31December 2009 at the Liverpool site

Elements (ng/m ³)	Average	Median	SD	Max.
Н	337	230	382	7 050
Na	301	214	345	2 570
Al	32	14	163	5 260
Si	105	52	464	15 060
Р	7.8	3.1	79	2 700
S	446	364	311	2 560
Cl	280	163	340	2 540
К	82	55	116	3 050
Ca	35	28	50	1 540
Ti	6.0	3.2	35	1 180
V	0.6	0.4	1.1	30
Cr	0.6	0.5	0.6	7
Mn	3.2	2.1	7.8	250
Fe	82	52	362	12 230
Со	0.6	0.3	2.5	83
Ni	0.4	0.3	0.6	8
Cu	3.1	2.2	3.3	39
Zn	20	12	25	230
Br	7.1	3.4	13	165
Pb	16	5.8	29	390
Mass (µg/m³)	9.32	7.24	10.97	308
BC (μg/m³)	1.65	1.28	1.22	9.55
Soil (µg/m³)	0.60	0.34	2.52	83
Sea Salt (µg/m³)	0.76	0.54	0.88	6.52
nssS (µg/m³)	0.42	0.34	0.30	2.47
Ammonium Sulphate (μg/m ³)	1.84	1.50	1.28	10.5
Organics (µg/m ³)	2.50	1.26	4.08	77
RCM (µg/m ³)	7.42	5.98	6.51	150
RCM (%)	82	81	12	

Note the high standard deviations given in Table 1 were due to the seasonal variations of each of the parameters and not the intrinsic measurement errors which were typically between 10% and 15% of the average measured value (Cohen et al., 2002).

Calculations from the data in Table 1 show that the average composition of the $PM_{2.5}$ fraction measured at Liverpool between July 1998 and December 2009 was: (23±13)% ammonium sulphate, (22±16)% organics, (19±8)% black carbon, (11±12)% sea salt and (5.9±5)% windblown soils. The non–sea salt sulphur component was (93±8)% of the total sulphur showing that most fine sulphur was anthropogenic and not sourced from windblown sea spray.

4. PMF Source Apportionment

The compositions given in Table 1 can tell us a little bit about the sources of $PM_{2.5}$ at the Liverpool site, for example soils are around 6% and sea salt around 11% of the total fine mass. However for full quantitative source fingerprints, and their contributions to the total fine mass, we turn to standard positive matrix factorisation (PMF) techniques. These have been fully described by Paatero and Tapper (1994). Basically the *m* by *n* data matrix *X* is represented by the product of an *m* by *p* fingerprint matrix *F* and a *p* by *n* contribution matrix *G* with an *m* by *n* error matrix *E*, namely:

$$X = F.G + E \tag{1}$$

where the error matrix E is minimised through a penalty function Q (Cohen et al., 2010) under the constraint that the factor elements remain greater than zero. The expected value of Q is:

$$Q = nm - p(n + m) \tag{2}$$

where m is the number of measured chemical species, n is the number of sampling days, p is the number of unique factors or sources identified from the PMF process.

PMF analysis was performed using the IBA elemental data with m=21, and n=1.081 "good" sampling days. For this study 89 daily "bad" sampling days were rejected as being not representative of the average source contributions required. The aim was to use PMF techniques to try and find average source fingerprints and their contributions to the total fine gravimetric mass. Extreme outlier events affect the final PMF solution significantly. To overcome this we ran the PMF codes through the full dataset and then measured the distance between each of the daily points and the line of best fit to the PMF mass versus the gravimetric mass plot. All points that were more than 5 standard deviations away from the average distance were removed after which the PMF analysis was re–run. The removed points were the "bad" non representative points mentioned above.

The expected Q_{exp} is 14 987 when p=7 factors or source fingerprints, with none of the 21 elements used being "pulled down" or adjusted in any way (Paatero and Tapper, 1994). The actual Q for this 7 factor calculation was 13 284 or 0.89 of the expected Q, which was considered satisfactory.



Figure 2. PMF source factors F1–F7 or fingerprints for Liverpool from July 1998 to December 2009 inclusive, where each of the elemental contributions are normalised to a value of 1.0 for the maximum element in that factor.

Figure 2 shows the source fingerprints obtained from the *F* matrix of Equation (1) with *p*=7 and *m*=21. These are discussed individually later. Figure 3 shows the sum of these seven source contributions (PMF) compared with the total $PM_{2.5}$ gravimetric mass (Mass). The agreement is excellent as demonstrated by the almost complete overlap of the two curves in Figure 3. All basic seasonal and daily trends during the full 11 year study period were well reproduced.



Figure 3. Comparison of PMF mass with gravimetric mass for 7 factors fit to data from 1 July 1998 to 31 December 2009.

As mentioned above no elements were artificially "pulled down" using the *F*key matrix notation of Paatero and Tapper (1994).

Six, seven and eight PMF factor solutions were considered. Each solution was then tested with values of Fpeak between -0.2 and +0.2 and small changes to the errors on elemental measurements were also made to try and find a solution with factors that better identified possible source fingerprints. The 7 factor solution, while the Q value was 0.89 of the expected value, better satisfied this requirement and did not require "pulling down" of elements by using the Fkey techniques in PMF. Also no correlation of the columns in the G matrix was observed. An eight factor solution reduced the Q value even further and several of the factors found were unable to be identified with logical known recognisable source fingerprints. With six factors several of the sources were obviously combined and again difficult to differentiate. Based on this the seven factors are presented and for the later discussion like factors are added together to provide a combined contribution. That is, while there were two separate Auto sources the combined fingerprint contributions were considered to be the best achievable with the present data set. Identifying more than the 21 chemical species currently identified in the filter samples would overcome some of the difficulties. For example, including neutron activation analysis as well as the IBA analysis can potentially identify another 20 elements which would considerably enhance the source fingerprints and the PMF analyses. However this was beyond the scope of the current study.

Each of the seven fingerprints and the reason for their names are discussed below.

Factor 1; was dominated by the grouping of Zn, Br, Pb, BC and H which is typical of automobiles using leaded petrol pre to 2001. It was labelled *Auto2*, consistent with the range of elements found by Kim Oanh et al. (2010).

Factor 2; was dominated by high Na, S, and BC but no Cl. We believe this represents aged sea spray where the high sulphate content has replaced the Cl in NaCl. It represents air masses that have spent some time circulating in the Basin after being blown in from the ocean. It was labelled *Sea2*, Cl depleted sea salt (Qin et al., 1997).

Factor 3; was dominated by high H, K, BC with tracers of soil and clearly represented biomass burning and vegetation burning

common in domestic heating in the winter time and bush fire smoke in the summer months. It was labelled *Smoke*, consistent with elements found by Lee at al. (2008).

Factor 4; was dominated by high Al, Si, K, Ca, Ti, Mn and Fe and was low in H, BC and S and clearly represented fine windblown soils (Cohen et al., 2010). It was labelled *Soil*.

Factor 5; was dominated by high BC, Fe and H. There were significant numbers of cars, buses and trucks close to the site and we believe this fingerprint is representative of modern motor vehicles not running on leaded petrol which was phased out in the Sydney Basin by 2001. It was labelled *Auto1*.

Factor 6; was dominated by high S, H and BC and the ratio of H to S supported this fingerprint as being representative of secondary sulphate (Kim et al., 2004). It was labelled *SndryS*.

Factor 7; was dominated by high Na and Cl with traces of H and Ca, it appeared to have no sulphate present and therefore represented sea salt rather well although the Cl/Na ratio was significantly greater than the expected 1.54 for pure sea spray. The reason for this larger value could be due to the presence of other chorine containing compounds (not containing Na) like ammonium chloride or calcium chloride which would raise the Cl levels above those expected for NaCl. It was labelled *Sea1*, which is in agreement with "fresh marine" source reported by others (Qin et al., 1997).

The time series plots for these fingerprints are given in Figure 4. Clear summer–winter seasonal variations were present in all fingerprints except *Soil*. The *Auto2* factor shows a decline after 2001 with the reduction of leaded petrol usage, whereas *Auto1* shows an increase.



Figure 4. The percentage PMF source contributions to the total $PM_{2.5}$ mass for the seven source fingerprints for the Liverpool site between 1 July 1998 and 31 December 2009.

The seasonal variability in the *Smoke* fingerprint was particularly obvious, being higher in the winter months than in the summer due to the large number of domestic wood heaters being used in the cooler winter months. This factor represented around 40% of the fine fraction in winter dropping to nearly zero in the summer. Clearly wood heaters in the Liverpool area in winter are a major source of fine particle pollution.

Secondary sulphur showed the opposite seasonal variations to smoke being higher in the summer when UV, sunlight, higher temperatures and the humidity are more favourable to its production than in the winter months.

Table 2 shows the average fingerprint contributions to the fine particle mass estimated from the PMF calculations for summer (December to February) and winter (June to August) seasons. These values are consistent with the average composition of Table 1 except for the sea salt estimates. The *Auto1* and *Auto2* contributions have been added together to produce a total *Auto* value in Table 2. The *Sea1* and *Sea2* values were not added together as the seasonal variations for the smaller *Sea1* factor were not as strong as for the larger *Sea2* factor.

The average for the study period for the PMF estimate for sea salt (by adding both *Sea1* and *Sea2* contributions together) was 22% ranging between 36% in the summertime and 12% in the wintertime. This was nearly twice the 11% estimate of fresh sea salt (NaCl) calculated from the data in Table1. The PMF aged sea salt component (*Sea2*) was associated with large amounts of BC and S significantly raising the total sea salt estimate. This was consistent with transport and industrial emissions near the coast mixing with afternoon sea breezes over a period of several days, particularly in the Sydney summertime, and then being transported in a westerly direction inland towards the Liverpool site.

5. Long–Range Soil Transport into the Basin

With 4.5 million people and nearly 3 million motor vehicles in the Sydney Basin area we expect most of the fine particle pollution to be generated within the Basin. However there is reason to believe that some of these sources can originate from outside the Basin, particularly wind-blown soils from major desert dust storms in central Australia (McTainsh et al., 2005). To test this further we look at significant outlier events in the time series records of related elemental concentrations.

Malm et al. (1994) defined fine soil as combination of the oxides of Al, Si, Ca, Ti and Fe. We use this to plot the time series estimates of soil for the Liverpool site in Figure 5 from January 2001 to 31 December 2009. During this period there were 31 outlier soil event days which were higher than $1.7 \,\mu g/m^3$ or more than 5 times the median soil value at Liverpool. Some of these, like the 27 November 2002 shown on Figure 5, were associated with known desert dust storms. Indeed, a major desert dust storm hit the Sydney Basin on 23 September 2009 with soil levels reaching to

 $83 \ \mu g/m^3$ at Liverpool, off the top of the graph of Figure 5. Our aim here is to see how many of these outlier events can be ascribed to long–range desert dust transport into the Basin.



Figure 5. Estimated soil from the sum of the oxides of AI, Si, Ca, Ti, and Fe for the Liverpool site between January 2001 and December 2009.

In Figure 6, a rectangle has been drawn to represent each of 14 main desert regions across Australia. Clearly deserts cover a significant fraction of inland Australia. The 15th rectangle in south eastern Australia represents a key agricultural region in New South Wales called the Riverina area. This area is regularly farmed and irrigated and is a major food bowl for much of eastern Australia. It has been included along with the desert regions to assess the relative impacts of farming and desert dust transport on the Liverpool site and hence the Sydney Basin.



Figure 6. Seven day back trajectory intersections from Liverpool with 15 desert regions in Australia between January 2001 and December 2009 and a 7 day hourly back trajectory for a high soil event on 4 September 2002.

 Table 2. Average PMF source contributions (%) to the total PM_{2.5} mass for the Liverpool site for each summer and winter season between 1 July 1998 and 31 Dec 2009

	Summer				Winter			
PMF	Average	Median	SD	Max.	Average	Median	SD	Max.
Sea1	12	7	12	50	7	5	8	53
Sea2	24	24	11	52	5	1.9	7	36
SndryS	32	30	17	73	13	11	8.3	52
Auto	17	15	10	50	28	26	10	56
Soil	3.6	1.9	5.4	53	2.8	2.0	3.1	31
Smoke	12	11	10	45	45	45	13	71

Table 3 gives the names, longitude, latitude and the average distance from the Liverpool site for each of the rectangular regions in Figure 6. Note this is not a comprehensive list of desert regions within Australia but it is representative of possible regions that may contribute to dust in the Sydney Basin. Some desert regions are up to 3 000 km from the sampling site and most are more than 1 000 km away. The ±Lat and ±Long columns represent the extent of the rectangle used to represent these desert regions about their midpoints. Note that in this part of the globe 1 ° represents about 100 km.

Table 3. Significant dust source regions in Australia and their distance from

 the Liverpool site in the Sydney Basin

#	Dust source	Lat	±Lat	Long	±Long	Distance (km)
1	Lake Mungo	-33.8°	1°	144.1°	1°	660
2	Lake Windaunka	-31.0°	1°	142.7°	1°	860
3	East Flinders	-29.9°	1°	139.6°	1°	1 200
4	Olympic Dam	-31.0°	1°	136.5°	1°	1 420
5	Emu Fields Salt Pans	-29.1°	1°	133.6°	1°	1 750
6	Lake Eyre North	-28.0°	1°	137.5°	1°	1 450
7	Simpson Desert	-24.0°	1°	137.4°	1°	1 730
8	Great Victoria Desert West	-28.0°	1.5°	124.5°	2.5°	2 030
9	Great Victoria Desert East	-28.0°	1.5°	131.0°	2.5	2 630
10	Gibson Desert	-25.0°	1.5°	126.0°	1.5°	2 620
11	Little Sandy Desert	-24.0°	1	122.0°	1.5°	3 030
12	Great Sandy Desert West	-21.0°	1.5°	124.0°	2.5°	3 030
13	Great Sandy Desert East	-24.5°	1°	130.5°	1°	2 560
14	Tanami Desert	-21.0	2	131.0	2	2 440
15	Riverina agricultural	-34.7	0.6	146.5	1.8	470

The PC version of HYSPLIT v4.8 (HYbrid Single–Particle Lagrangian Integrated Trajectory; Draxler and Rolph, 2003) was used to generate a database of back trajectories for every hour of every sampling day during the study period. Two starting heights of 300 m and 500 m were chosen to reduce topographic effects on the simulations, and to be within the atmospheric boundary layer for most sampling days. In comparing HYSPLIT calculated trajectories with tracer gas releases, Draxler (1991) estimated that the model error is between 20% and 30% of the travel distance. For this reason, we have restricted back trajectories to seven days along each trajectory and the study area to latitudes -50° to -10° and longitudes 110° to 170° . This area includes all the desert regions described and shown in Figure 6.

A FORTRAN code was written to sort the HYSPLIT output files and to identify each of the back trajectories out of Liverpool for every hour for every sampling day which passed through each of the rectangular regions identified by position and size in Figure 6 and Table 3. Figure 6 also shows 24 hourly back trajectories for the high soil day ($4.53 \ \mu g/m^3$ soil or 36% of PM_{2.5} mass) on 4 September 2002. On this day the back trajectories left the Liverpool site travelling west across Lake Windaunka (2), the East Flinders (3) ranges and Olympic Dam (4) and after crossing the Great Victoria Desert (8) reached Perth and the Western Australian coast. The closer back trajectory path lengths crossing Lake Windaunka (2) and the East Flinders (3) ranges were typically 1 000 km and 30 hours from the Liverpool site. The trajectories to Perth were more than 3 400 km long and more than 70 hours from Liverpool.

For each trajectory passing through any of the rectangles, the average position between the entrance and exit of the trajectory was plotted as a point within that rectangle. The number of such intersection points within each rectangle was then representative of the relative impact of each soil source region on the Liverpool sampling site during the nine year study period from 2001 to 2009 inclusive. HYPSPLIT back trajectories prior to January 2001 were not available and so soil data between 1998 and 2000 inclusive were not used.

For the 921 sampling days (midnight to midnight) between January 2001 and December 2009 there were 44 208 hourly back trajectories from the Liverpool site for the two starting heights of 300 m and 500 m. Of these about 1.85% back trajectories originated from either 300 m or 500 m starting heights with soil greater than $1.7 \,\mu g/m^3$. The full details are given in Table 4 for both starting heights and sorted in decreasing number of back trajectory intersections per source rectangle.

Table 4. Seven day back trajectory intersections from Liverpool with 15 dust regions in Australia between January 2001 and December 2009 for fine soil events greater than 1.7 μg/m³ with starting back trajectory heights of 300 m and 500 m

300 m	Intersections with soil> 1.7 μg/m ³	Intersection (%)	500 m	Intersections with soil> 1.7 μg/m ³	Intersection (%)
15 Riverina	283	34.6	15 Riverina	266	32.6
1 LakeMungo	199	24.3	1 LakeMungo	191	23.4
2 LakeWindaunka	105	12.8	2 LakeWindaunka	120	14.7
3 EastFlinders	64	7.8	3 EastFlinders	66	8.1
4 OlympicDam	41	5.0	4 OlympicDam	53	6.5
5 EmuFieldsSalt	29	3.5	9 GreatVicE	31	3.8
6 LakeEyreNorth	28	3.4	5 EmuFieldsSalt	30	3.7
9 GreatVicE	27	3.3	6 LakeEyreNorth	16	2.0
8 GreatVicW	23	2.8	10 Gibson	16	2.0
10 Gibson	6	0.7	8 GreatVicW	9	1.1
14 Tanami	5	0.6	14 Tanami	6	0.7
13 GrtSandyE	4	0.5	13 GrtSandyE	5	0.6
7 SimpsonDesert	3	0.4	11 LitSandy	4	0.5
11 LitSandy	1	0.1	12 GrtSandyW	3	0.4
12 GrtSandyW	0	0.0	7 SimpsonDesert	1	0.1
Total intersections	818			817	

The most interesting aspect of Table 4 was that the rectangle with the most intersections for outlier days with soil above $1.7 \,\mu g/m^3$ was the Riverina area for both 300 m and 500 m starting heights. This agricultural region was 470 km from the Liverpool site and contributed to about one third of total outlier soil events as measured at the Liverpool site. Lake Mungo (1), Lake Windaunka (2), the East Flinders ranges (3) and Olympic Dam (4) were also significant contributors being between 600 and 1 500 km from the Liverpool site.

Table 5 shows the dates, PM_{2.5} masses and soil contributions for the 24 outlier events with starting back trajectory heights of 300 m and the 28 outlier events for heights of 500 m during January 2001 and December 2009. It also shows the number of hourly trajectories in each 24 hour sampling period that had intersections with at least one of the rectangular source regions plotted in Figure 6. Obviously days with the number of trajectory intersections approaching 24 (the maximum number) have a higher potential to contribute to long–range transport of soil from these desert regions. Clearly, if very few trajectories on a given day intersect with desert source regions then the high soil measurement in the Basin is most probably due to local soil events and not long–range transport.

Table 5. The dates, $PM_{2.5}$ masses and soil contributions for the 24 outlier events with starting back trajectory heights of 300 m and the 28 outlier events for heights of 500 m during January 2001 and December 2009

Date	Number of 300 m trajectories in 24 hrs	Number of 500 m trajectories in 24 hrs	Mass (µg/m³)	Soil (µg/m³)	Soil (%)
6/6/2001	20	19	41.3	2.16	5.2
26/12/2001	24	24	62.8	1.90	3.0
2/1/2002	24	24	48.7	1.97	4.0
14/7/2002	13	20	42.2	1.76	4.2
4/9/2002	24	24	12.5	4.53	36.3
23/10/2002	23	24	20.4	3.29	16.1
3/11/2002	15	9	31.6	3.28	10.4
13/11/2002	5	11	12.7	1.88	14.9
27/11/2002	14	17	15.2	7.05	46.4
2/6/2004	9	7	29.3	2.66	9.1
9/6/2004		9	22.6	1.92	8.5
16/6/2004	14	11	29.0	3.17	10.9
23/6/2004	4	5	22.1	1.97	8.9
30/6/2004	24	24	14.7	1.89	12.9
4/7/2004	10	13	15.4	1.86	12.1
8/6/2005	17	4	36.4	3.66	10.1
12/7/2006	21	19	18.0	1.79	10.0
20/9/2006	7	8	6.4	2.08	32.5
24/9/2006	11	10	8.4	2.87	34.1
22/11/2006		2	42.8	3.19	7.4
27/5/2007	20	17	23.1	1.81	7.8
25/7/2007		6	24.4	2.20	9.0
15/4/2009	23	24	12.9	7.08	55.1
19/8/2009		1	26.3	2.12	8.1
23/9/2009	21	20	308.4	83.45	27.1
14/10/2009	24	24	4.5	2.64	58.7
22/11/2009	10	8	19.0	5.68	30.0
29/11/2009	23	20	20.4	11.91	58.3

6. Conclusion

IBA techniques have been applied to measure 21 different chemical species present in fine particle ($PM_{2.5}$) pollution at Liverpool in the Sydney Basin between July 1998 and 31 December 2009. The average composition was found to be (23±13)% ammonium sulphate, (22±16)% organics, (19±8)% black carbon, (11±12)% sea salt and (5.9±5)% wind–blown soils.

The dataset obtained was large enough and the mass closure sufficient (82±12)% to apply positive matrix factorisation (PMF) techniques to obtain seven source fingerprints related to motor vehicles (23±11)%, secondary sulphates (24±21)%, biomass burning (27±25)%, sea salt (22±16)% and windblown soils (3.7±5.5)% and to estimate their contributions to the total fine mass (PM_{2.5}). The straight IBA soil estimates were higher than the PMF estimates as they assume that all the silicon was associated with soils, whereas the PMF techniques had silicon in several other non soil fingerprints as well. Similar arguments can be used to explain the differences between the IBA sea salt and the PMF sea salt estimates where elements other than just Na and Cl also occurred in the PMF sea salt fingerprint.

Of the 921 sampling days between 1 January 2001 and 31 December 2009, HYPSLIT back trajectory techniques identified 28 of the 31 daily high outlier soil events measured at Liverpool as originating from source areas outside the Sydney Basin. The Riverina (15) agricultural region, some 470 km to the southwest of the Sydney Basin, was the major contributor (33%) to these outlier soil events (> 1.7 μ g/m³) affecting the Liverpool site. The remaining outlier soil events originated from desert regions between 600 and 1 500 km to the west of Sydney. This was a clear demonstration of long–range fine particulate dust transported into the Sydney Basin.

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