SOURCES AND PROCESSES THAT INFLUENCE PARTICLE SIZE, NUMBER AND MASS AT A RURAL SITE IN ENGLAND (HARWELL)

Aurélie Charron[1], Wolfram Birmili[2] and Roy M. Harrison[1]

Division of Environmental Health & Risk Management
School of Geography, Earth & Environmental Sciences
The University of Birmingham
Edgbaston, Birmingham B15 2TT

[2]Leibniz Institute for Tropospheric Research
"Tropospheric Aerosols: In-situ Characterisation, Processes, and Climatology"
Permoserstrasse 15, 04303 Leipzig, Germany

Report to DEFRA prepared by the University of Birmingham and Casella Stanger under contract EPG 1/3/184 "Monitoring of Airborne Particulate Concentrations and Numbers in the UK".

Content List **Page**

SUMMARY

- Sources and processes that influence particle size, number and mass at Harwell are examined using a large dataset combining different particle metrics, gas concentrations and meteorological data. This report is an interim report and many issues discussed need further examination.

- The influence of many meteorological parameters is studied. As expected, $PM_{2.5}$ and the numbers of particles with diameters above 30 nm are significantly reduced by increasing wind speed, unstable atmosphere and a well mixed atmospheric boundary layer.

- Consistent with their possible different modes of production, PM_{coarse} and particles with diameters below 30 nm show different behaviour to the other particle metrics.

- Dry, warm and sunny weather strongly favours PM_{coarse} concentrations, which are apparently unaffected by the wind speed. This suggests that the wind-blown resuspension process (favoured by warm and dry weather) and the dispersion due to the wind may compensate for each other. High PM_{coarse} concentrations are associated both with winds blowing from polluted and "clean" sectors in agreement with possible anthropogenic and non-anthropogenic contributions.

- Numbers of particles with diameters below 30 nm are also favoured by dry, warm and sunny weather (higher global insolation). Their concentrations seem to be unaffected by the wind speed while as at Marylebone Road, the wind speed generates a shift of the size distribution to finer diameters. Additionally, numbers of particles below 30 nm are favoured by a well mixed atmospheric boundary layer. These particles also show an average daily cycle with concentrations higher the afternoon, which is opposite to integrated counts above 30 nm that show daily cycles driven by the diurnal cycle of the boundary layer. Finally, high numbers of particles with diameters below 30 nm are also associated with winds blowing from "clean" sectors. These results suggest that some photochemically produced particles are measured at Harwell.

- Harwell is a "receptor site" influenced by densely populated areas such as London and local anthropogenic sources such as Didcot Power Station. In particular, results indicate that vehicle emissions influence particle numbers and mass at Harwell when the wind

blows from SE directions. However, the local A34 road contribution and the meso-scale transport from London cannot be separated.

- Didcot Power Station, located 7 km away, is clearly seen as a source of high SO_2 and particle mass concentrations at Harwell. A few events of high numbers of small particles associated with very high SO_2 concentrations and winds blowing from NNE directions are observed at Harwell. All except one were short-lived episodes. This suggests that sporadic nucleation events occur in the SO_2-rich plumes from Didcot Power station.

- Methods have been developed in order to identify large-scale new particle events observed at Harwell, and in order to relate them to air and aerosol properties (gas concentrations, pre-existing surface area…), meteorological effects (solar radiation), and air mass/weather characteristics (trajectories/atmospheric stability).

- Large scale new particle formation events takes place predominantly in cool westerly maritime air masses from the northern Atlantic ocean. The typical situation observed on these days has air masses which are clean (low accumulation mode particles and NO_x concentrations). The weather is fair, warm, dry and a little windy and the solar radiation very high. When these cool and clean air masses arrived to the western coast of the UK, conditions seem to be favourable for nucleation (turbulent mixing of air masses with different temperature and humidity, high solar radiation, a mix of biogenic and anthropogenic gases, low pre-existing surface area).

1. BACKGROUND AND OBJECTIVES

At concentrations typical of those measured in urban areas, aerosols affect human health, whilst in the global atmosphere influenced by major pollution sources, aerosols have an important influence on the climate, both directly and indirectly. As a consequence, understanding the sources of aerosols in the atmosphere, their transformations, the factors that influence their concentrations and processes responsible for their removal from the atmosphere are key issues.

It is accepted that meteorology affects the particle size, number and mass of atmospheric aerosols. However, the mechanisms and their significance need further investigation. Important parameters would be wind direction and speed, radiation, precipitation, atmospheric transport and turbulence. Conversely, the size of the particles will control their dynamics and consequently their behaviour in the atmosphere. The behaviour of aerosols will also depend on their origin which determines their initial size, chemistry and concentration.

Most studies on particle number size distributions and new particle formation have focused on the coastal or marine environment or upon remote continental environments such as polar areas. Few studies have investigated areas with mixed influences very close to anthropogenic sources.

In this interim report, factors and sources that influence particle size, number and mass are investigated for a site located in southern England, in the vicinity of anthropogenic sources. An examination of upwind large-scale new particle formation is also conducted.

2. SAMPLING SITE AND INSTRUMENTS

2.1 Sampling Site

The monitoring station is within a self-contained, air conditioned housing located within the grounds of the Harwell Science Centre. The nearest road is for access to buildings within the science park only. The surrounding area is generally open with agricultural fields. The nearest trees are at a distance of 200 - 300 metres from the monitoring station.

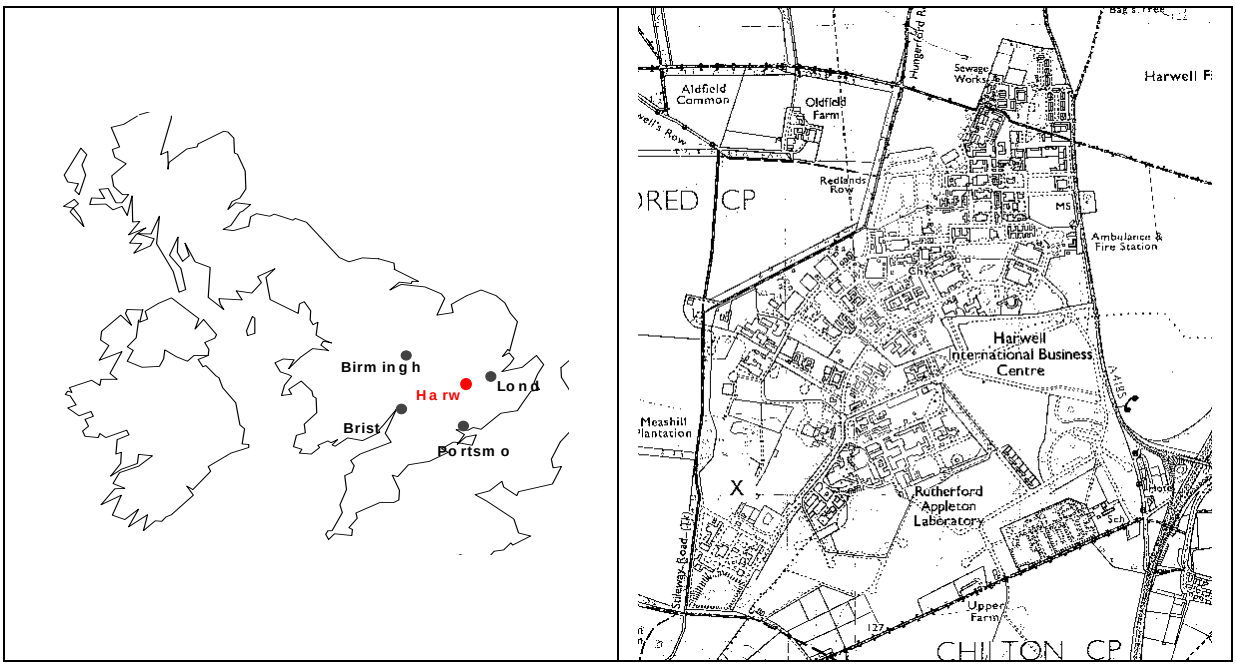


Figure 2.1: Location of Harwell Sampling Site (a) in the UK; (b) in Harwell Research Centre

2.2 Instruments

Particle size distributions are measured using a Scanning Mobility Particle Sizer (SMPS) which is a combination of an electrostatic classifier (Model 3071A, TSI) which separates the particle sizes into different fractions and a condensation particle counter (TSI Model 3022A) which measures their concentrations. Mobility distributions are inverted into particle number size distributions using TSI software version 2.5. Particle number size distributions in the particle size range 11-450 nm have been recorded at Harwell since 1998. Technical details on this instrument can be found in Wang and Flagan (1990). The Scanning Mobility Particle Sizer (SMPS) measures lower particle numbers than the nano-Scanning Mobility Particle Sizer (nano SMPS) at size diameters below 100 nm. The lower the particle diameter, the higher the divergence. Both the lower efficiency of the 3022A Condensation Particle Counter (SMPS) for smaller particles and larger losses by Brownian diffusion and diffusional broadening of small particle trajectories by the 3071A Differential Mobility Analyser (SMPS) could explain this result since size-dependent lower efficiencies and losses are not corrected by the SMPS software. The SMPS data used in this study are corrected for losses in the classifier using the 'classifier transfer function' established by Birmili et al. (1997) for the 3071A Differential Mobility Analyser. The classifier transfer function is presented in Annex 1.

Two Tapered Element Oscillating Microbalances (TEOM) are used to monitor PM_{10} and $PM_{2.5}$ particle mass concentrations. The two TEOMs are identical instruments (Model 1400AB) except for the design of the sampling heads. The particle mass is determined by continuous weighing of particles deposited onto a filter. The filter is attached to a vibrating

hollow tapered glass tube whose frequency changes as the mass loading on the filter increases. The vibration frequency is converted to mass concentrations by a microprocessor. Air at 16.67 L min^{-1} is sampled through the PM_{10} impactor inlet and divided between the filter flow (3 L min^{-1}) and an auxiliary flow (13.67 L min^{-1}). For $PM_{2.5}$ measurements, the TEOM is fitted with a URG $PM_{2.5}$ cyclone inlet. The inlet of the TEOMs is heated to 50°C prior to particles being deposited onto the filter in order to eliminate the effect of condensation or evaporation of particle water. This heating of the aerosol stream induces losses of semi-volatile species. TEOM and Partisol gravimetric data at Harwell are compared elsewhere (Charron at al., 2004). Differences between TEOM and Partisol filter-based gravimetric methods depend on the temperature, the relative humidity and on the concentrations of semi-volatile particulate compounds such as ammonium nitrate (Charron et al., 2004). The use of basic correction factors was not found adequate. From the PM_{10} and $PM_{2.5}$ measurements, the PM_{coarse} fraction corresponding to the mass of particles between 2.5 μm and 10 μm has been calculated by difference.

2.3 Data Used

A very large dataset from February 1999 to December 2001 is used for this study. 12,453 hourly SMPS data and 19,281 hourly $PM_{2.5}$, 21,813 hourly PM_{10} data were available.

Harwell is also equipped with continuous monitors measuring trace gases, including VOCs and NO_x concentrations. Data are available from the UK Air Quality Archive (http://www.airquality.co.uk).

Meteorological data from the Benson station and backwards trajectories were supplied by the British Atmospheric Data Centre. The wind speed, wind direction, the temperature, the dew point (used to compute the relative humidity), the rain amount and the total cloud amount are meteorological parameters that are available on a hourly basis. Daily global insolation amounts are also available.

The following parameters are examined:

- **Temperature** is an important parameter. Lowering the temperature leads to a lowering of the equilibrium vapour pressure above the aerosol resulting to the transformation of gaseous compounds to the liquid or solid phase.

- **Relative humidity**: High relative humidity would favour homogenous binary nucleation of sulphuric acid and water (Easter and Peters, 1994). On the other hand, ternary nucleation involving ammonia is expected to be independent of relative humidity (Korhonen et al., 1999) and is probably the most relevant process.

- **Wind speed** is also studied since it was found as an influential factor on particle numbers and sizes at Marylebone Road and it is expected to influence particle mass.

- **Wind direction** will allow the examination of sectors associated with polluted air masses and the examination of whether new particle formation is associated with a specific sector. Väkeva et al. (2000) have shown that the wind direction is the most important meteorological factor affecting aerosol particles in Finland. Backward air masses trajectories will also be analysed.

- **Rain data** and the rain amount might influence particle numbers, pre-existing particle numbers, particle surface area and particle mass.

- **Particle surface area (PSA)** might be an influential factor since nucleation and condensation onto existing particles are competitive processes. However, some studies have not found any link between low PSA and nucleation. On the contrary, rather high PSA were measured days of nucleation events (Harrison et al., 2000; Birmili and Wiedensohler, 2000). The PSA is computed from SMPS data assuming spherical particles.

- **SO_2**: Oxidation of sulphur dioxide leads to formation of sulphuric acid leading to binary nucleation with water vapour (Easter and Peters, 1994) or ternary nucleation involving water vapour and ammonia (Korhonen et al., 1999). A clear link between SO_2 and events of new particle formation was observed by Birmili and Wiedensohler (2000). Because rates of new particle formation exceed theoretical rates, NH_3 is thought to be involved in new particle formation. Observations are in agreement with this assumption (Birmili et al., 2000; Harrison et al., 2000). Unfortunately, no NH_3 data are available.

- **NO_x** is an indicator of polluted air masses. In urban areas influenced by on-road emissions, high NO_x concentrations are associated with high numbers of particles.

- **Isoprene**: A recent paper (Claeys et al, 2004) has shown that gas-phase oxisation products of isoprene could lead to secondary aerosol formation. Additionally, the isoprene concentrations might possibly be correlated with other emissions of biogenic semi-volatile organic vapours. Biogenic semi-volatile organic vapours have been shown to be involved in homogeneous nucleation (e.g. Kavouras et al., 1998).

- **Global Irradiation Amount (GIA) and Total cloud cover (TCA), O_3** are variables of interest since photochemical processes are probably responsible for the formation of new particles.

3. RESULTS

3.1 Particle Mass, Numbers and Particle Size Distributions at Harwell

Table 3.1 presents the medians, 25 and 75 percentiles of concentrations measured at Harwell from February 1999 to December 2001. Figure 3.1 presents (a) the median and percentiles of particle number size distributions measured at Harwell and (b) median particle number size distributions associated with different influences.

	$PM_{2.5}$	PM_{coarse}	PM_{10}	$PM_{2.5}$: PM_{10}	$N_{(12\text{-}450)}$	$N_{(12\text{-}30)}$	$N_{(30\text{-}100)}$	$N_{(100\text{-}450)}$	O_3	NO_x	SO_2
	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	-	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	*ppbv*	*ppbv*	*ppbv*
25%ile	6.0	2.0	9.1	0.60	2165	421	1048	359	18.0	4.0	0
50%ile	9.0	3.7	12.7	0.72	3836	754	1949	677	26.0	7.0	0
75%ile	13.0	5.9	17.6	0.83	6040	1346	3207	1327	34.0	12.0	1

Table 3.1: Percentiles of hourly concentrations and ratio $PM_{2.5}/PM_{10}$ measured from February 1999 to December 2001

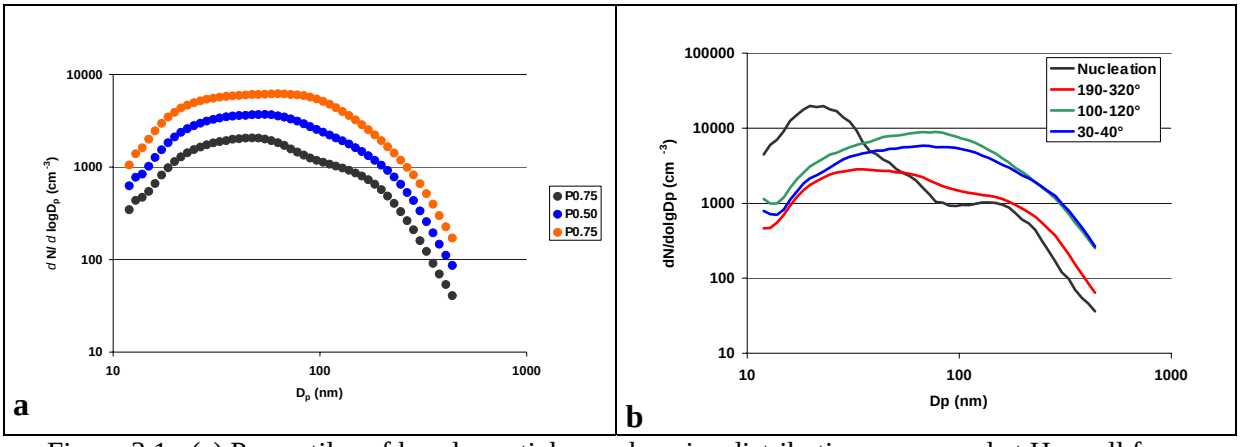


Figure 3.1 : (a) Percentiles of hourly particle number size distributions measured at Harwell from February 1999 to December 2001. (b) Average particle size distributions for nucleation events and for certain wind directions : 30-40° (Didcot Power Station + possible influence of traffic) ; 100-120° (A34 road and London direction) ; 190-320° (cleanest conditions). Log-log scale

Both Table 3.1 and Figure 3.1 show the high variability of particle numbers measured at Harwell.

The particle mass is mainly in the fine fraction (<2.5 µm) (ratios above 0.60 for 75% of data).

Higher particle numbers are generally measured within the 30-100 nm particle diameter ranges; but the highest, as well as the lowest, counts are measured within the 11-30 nm particle diameter range. These smaller particles actually show the greatest variability.

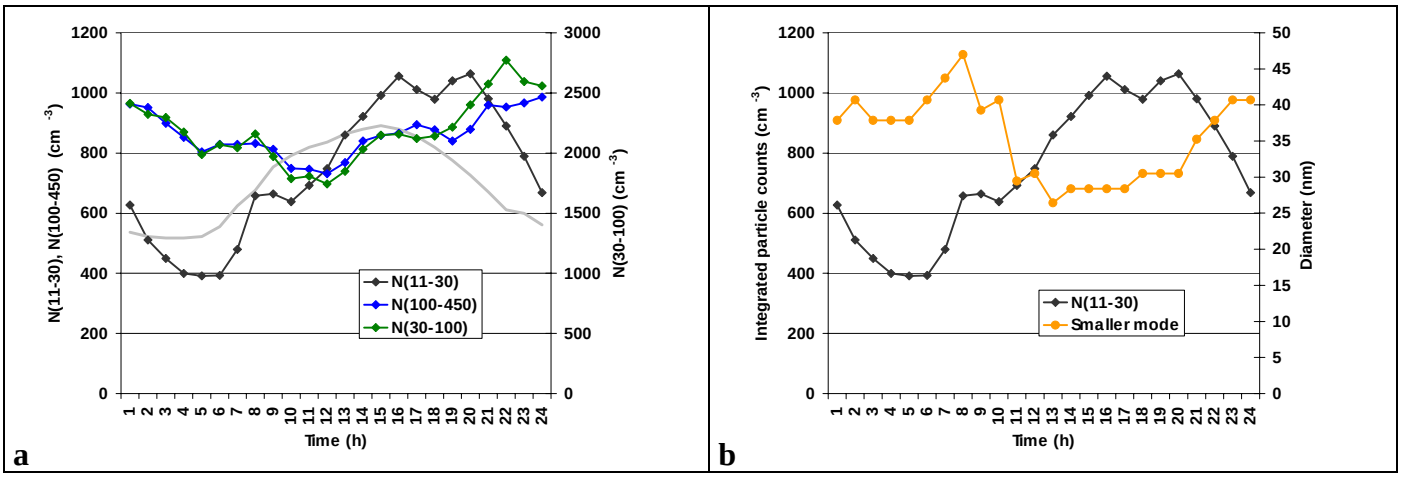


Figure 3.2 : (a) Median daily cycles of integrated particle counts for the ranges 11-30 nm, 30-100 nm and 100-450 nm. The median daily cycle of the temperature is presented on this chart. (b) Median daily cycles of the 11-30 nm integrated particle counts and of the smaller mode.

Figure 3.2 shows that integrated counts have daily cycles. The integrated counts between 30-100 and 100-450 nm (Figure 3a) have similar daily cycles with lower median numbers during the midday time periods in agreement with the diurnal behaviour of the boundary layer (mixed and convective during the day and stable during the night).

On the contrary, the integrated counts between 11-30 nm show higher concentrations during the daytime (afternoon) that are anticorrelated with the daily cycle of the smaller mode of particle number size distributions (figure 3.2b). The different behaviour of particles ranging from 11 to 30 nm suggests that these particles are from different processes than the others.

3.2 Variability Due to Meteorology

Many meteorological parameters are linked. For this reason, only data for the midday period (noon to 3 pm) are studied. This will tend to exclude any relationships between wind speed and other meteorological variables. Some meteorological parameters are studied together. The following meteorological parameters are studied:

- the wind speed (related primarily to the atmospheric pressure gradient);
- the temperature, relative humidity, global irradiation amount, total cloud amount are strongly correlated parameters and are studied together;
- the rainfall;
- the mixed layer depths.

3.2.1 *Influence of wind speed*

Stronger wind speed normally corresponds to lower pressure (cyclonic circulations), even though the influence is not so strong when only midday data are studied. The influence of other parameters are smoothed using medians of concentrations measured for each 1-knot wind speed bin (1 knot=0.515 m s^{-1}). Results are presented on Figure 3.3.

Similar to Marylebone Road, the effect of dilution and dispersion is clear for $PM_{2.5}$ and particles above 30 nm. The influence on numbers of particles above 30 nm is strong (factor 3 from 1 m s^{-1} to 9 m s^{-1}). As a consequence, the particle surface area and particle volume are strongly reduced by stronger wind speed. Similar to Marylebone Road, there is no influence of wind speed on particles below 30 nm.

In contrast to the urban sites of Marylebone Road and Bloomsbury, PM_{coarse} concentrations appear independent of wind speed. The wind-blown resuspension process and the dispersion due to the wind possibly compensate each other. This result suggests that resuspension processes are much less important at Harwell than for London where PM_{coarse} concentrations are strongly increased by the wind speed.

Decreasing concentrations of NO_x and SO_2 can also be seen with increasing wind speed. Not surprisingly, the wind speed does not influence photochemically-produced O_3.

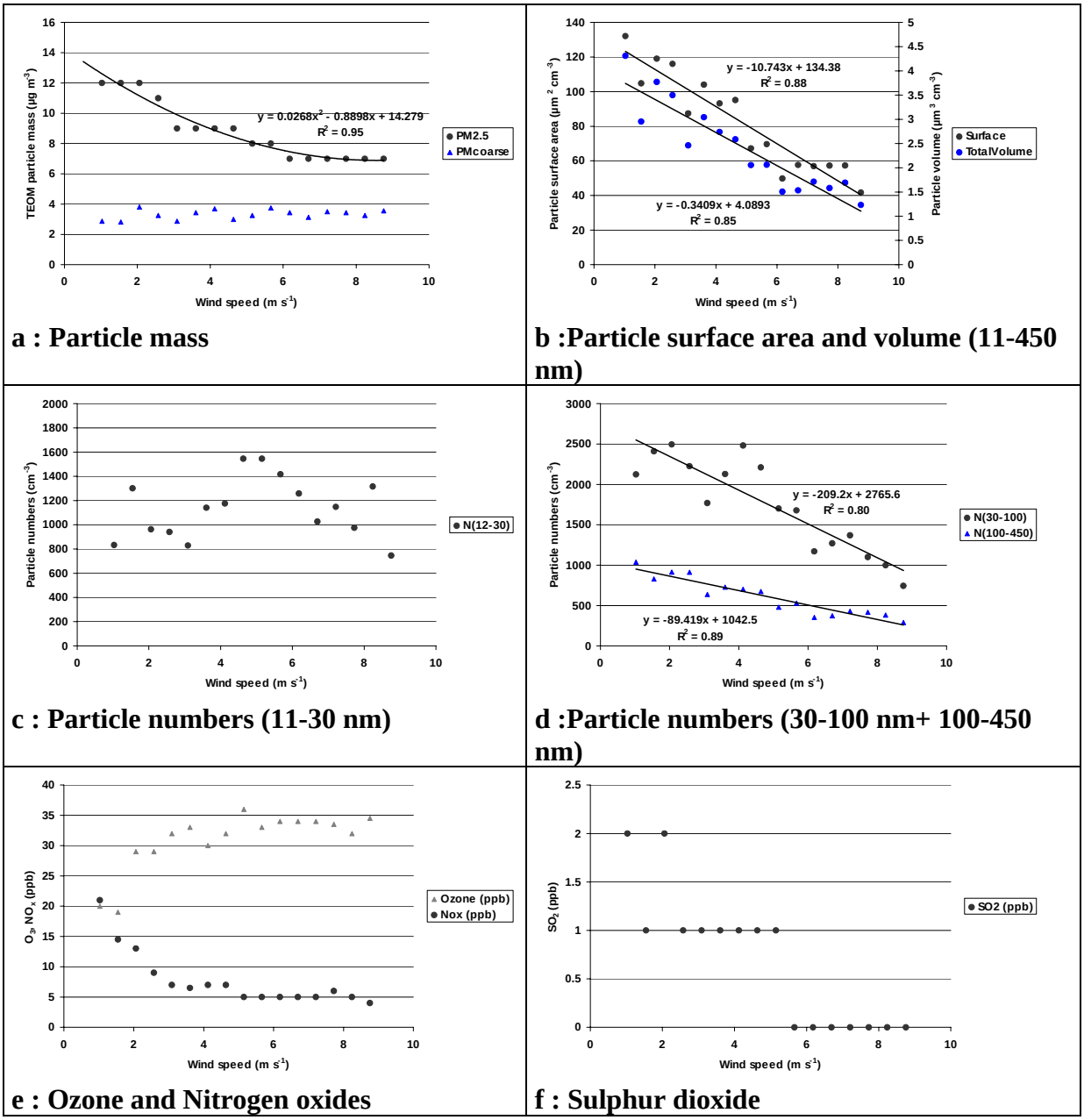


Figure 3.3: Median particle concentrations versus wind speed, for: $PM_{2.5}$ and PM_{coarse} particle mass, particle surface area and particle volume, integrated particle numbers

Similar to Marylebone Road, the diameter of the smaller mode decreases with the wind speed (Figure 3.4). The wind speed generates a shift of the size distribution to finer diameters.

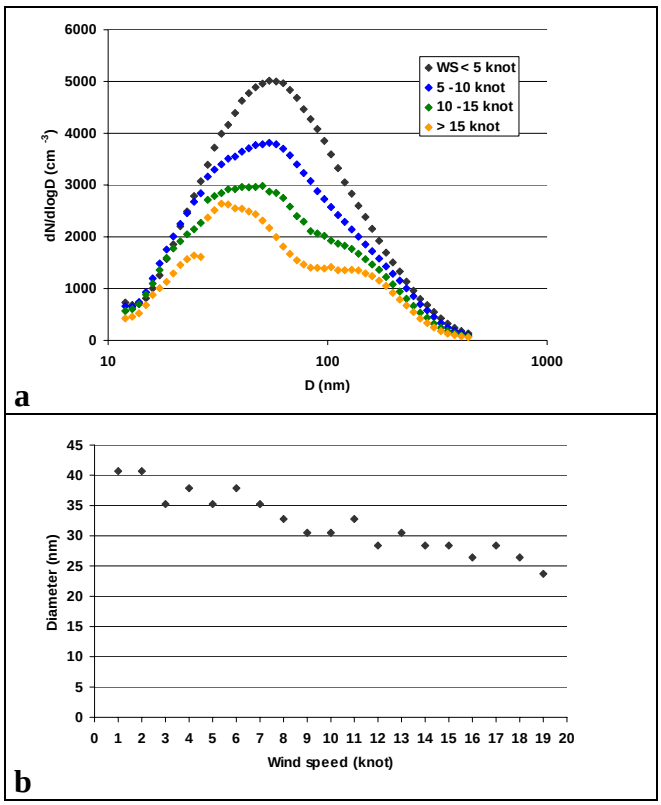


Figure 3.4: Influence of the wind speed on modal diameters.
(a) Particle number size distributions for 4 wind speed bins,
(b) smaller mode diameter vs. wind speed.

3.2.2 *Influence of the collinear Temperature, Relative humidity, Global Irradiation Amount and Total cloud amount*

Only the results with temperature are presented. The temperature and the relative humidity are anti-correlated and the temperature is positively correlated with the global irradiation amount and negatively correlated with the total cloud amount. Figure 3.5 presents the results.
These meteorological parameters do not show any influence on $PM_{2.5}$ and particle numbers above 30 nm. On the contrary, a strong relationship is found between the temperature (relative humidity, global irradiation amount) and the PM_{coarse} concentrations. This result indicates that dryer and warmer weather favours the resuspension of particles.

The temperature (relative humidity and global irradiation amount) weakly influences the numbers of particles below 30 nm. The smaller the particles, the stronger the influence (see results for 12.84 nm particles). This result may be the consequence of the influence of higher solar radiation on photochemically produced particles.

The influence of these parameters on the concentration of gases was also examined. The O_3 that is photochemically-produced also shows a weak relationship with the temperature (surprisingly, not a stronger relationship). Concentrations of NO_x strongly increase with

decreasing temperatures when the temperature is below 10 °C. For temperatures above 10°C, concentrations of NO_x do not seem to be influenced by the temperature. This result might possibly be attributed to larger emissions due to domestic heating during winter. On the other hand, the removal of NO_x via atmospheric reactions involving oxidants (e.g. OH) would be favoured by high irradiation amounts.

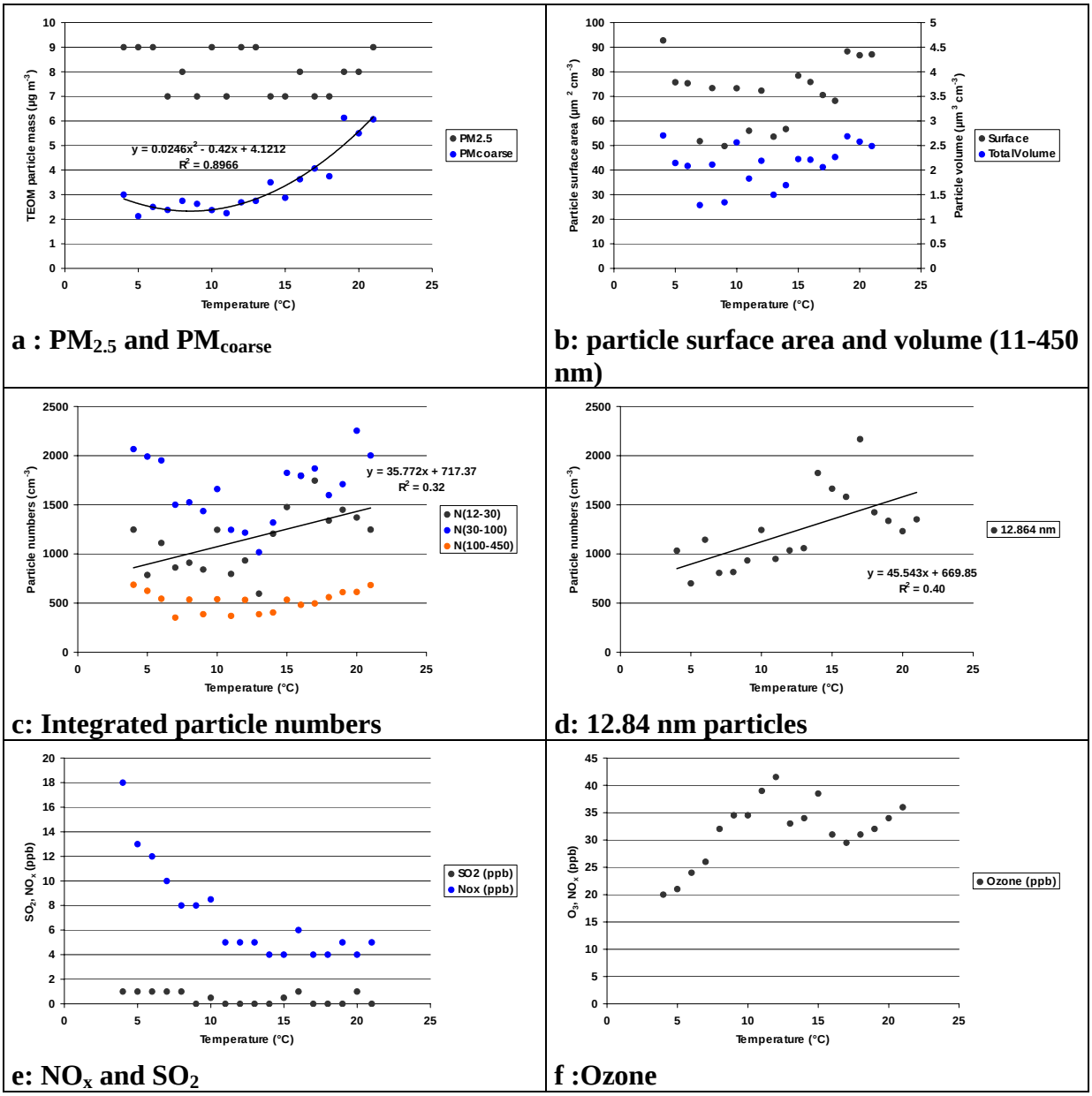


Figure 3.5 : Influence of the temperature on a : $PM_{2.5}$ and PM_{coarse} particle mass; b : particle numbers; c: NO_x and SO_2

3.2.3 *Influence of precipitation*

Concentrations measured during rain events and in the absence of rain are presented in Figure 3.6 as box plots. Not all meteorological parameters are smoothed. The relative humidity is higher when it rains (on average equal to 92%) than when it does not (on average equal to 82%). The atmospheric pressure is on average a little lower when it rains (1006 mb compared

to 1016 mb when it does not rain). The global irradiation amount is significantly lower when it rains (5347 kJ m^{-2}) than when it does not (9007 kJ m^{-2}).The influence of other parameters are smoothed (including the total cloud amount).

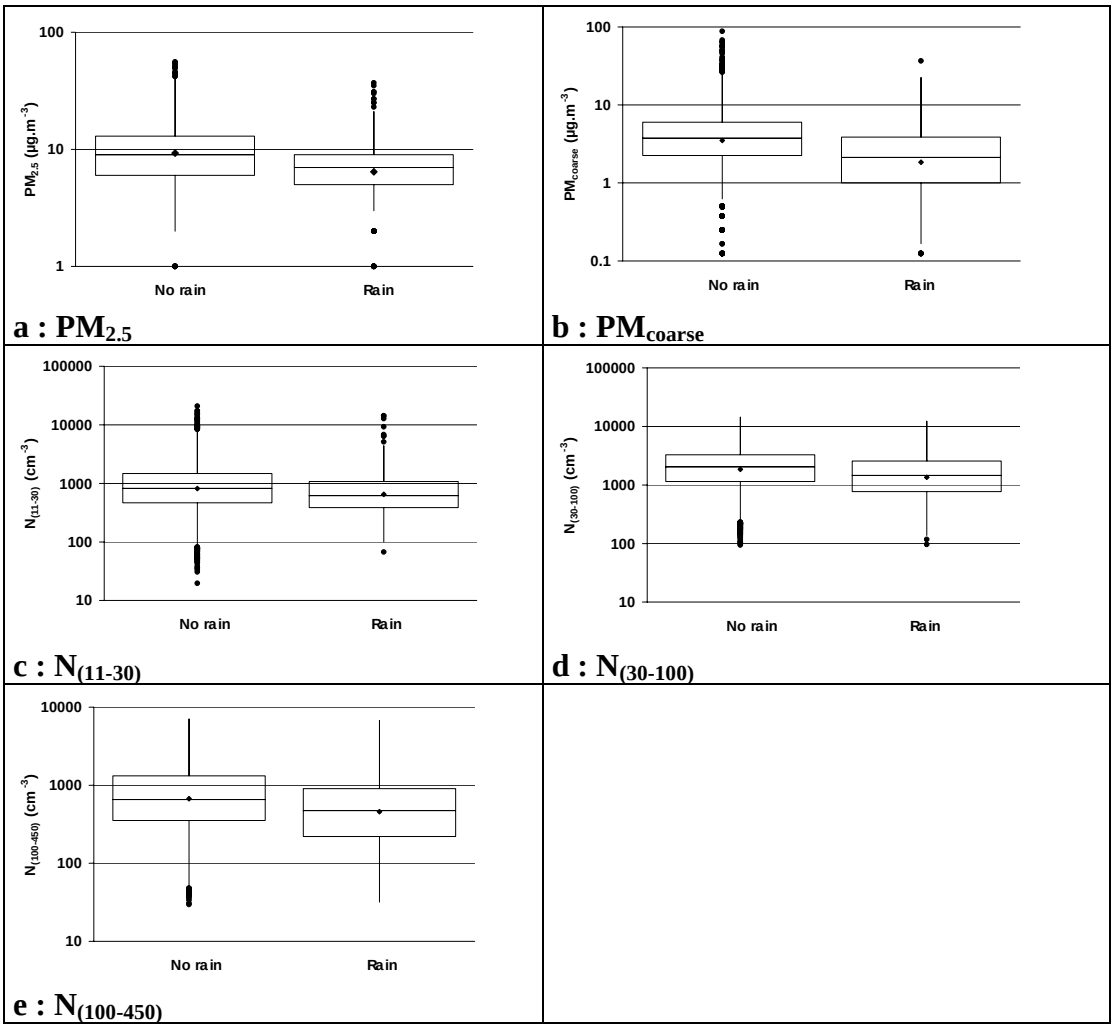


Figure 3.6 : Particle concentrations measured when it rains and when it does not, (a) : $PM_{2.5}$ particle mass ; (b):PM_{coarse} particle mass ; (c) : numbers of particles ranging from 11 to 30 nm ; (d) : numbers of particles ranging from 30 to 100 nm ; (e): numbers of particles ranging from 100 to 450 nm

Figure 3.6 presents the results. The influence of rain is more obvious at Harwell than at Marylebone Road (where the apparent washout effect is probably reduced by continuous on-road emissions). Higher concentrations are measured in the absence of rain for all particle metrics. The influence is stronger for particle mass than for particle numbers and stronger for larger particles (PM_{coarse}). The relationships with coarser and smaller particles may be influenced by other parameters : dryer weather for the PM_{coarse} and higher global irradiation amount for 11-30 nm particles (which are possibly not strongly affected by washout).

No relationship was found between the amount and the duration of rain and the concentrations measured.

3.2.4 *Influence of mixed atmospheric layer height*

Mixed layer heights (MLH) are calculated using the concept of a dry-adiabatically ascending air parcel and the radiosonde profiles available. Figure 3.7 presents the median particle number size distributions and median integrated counts for different MLH bins.

As expected, particle numbers in the accumulation mode are significantly higher when the MLH is lower as a result of a stable atmosphere and poor dispersion processes. Again, smaller particles behave differently since they are significantly higher when the MLH is higher. A nucleation mode seems to appear with increasing MLH. This results again suggests that these particles are not primarily emitted in the atmosphere but they are photochemically- produced. Note that higher MLH would be associated with, on the one hand, stronger wind speed and low atmospheric pressure, and on the other hand, lower cloudiness and higher solar radiation.

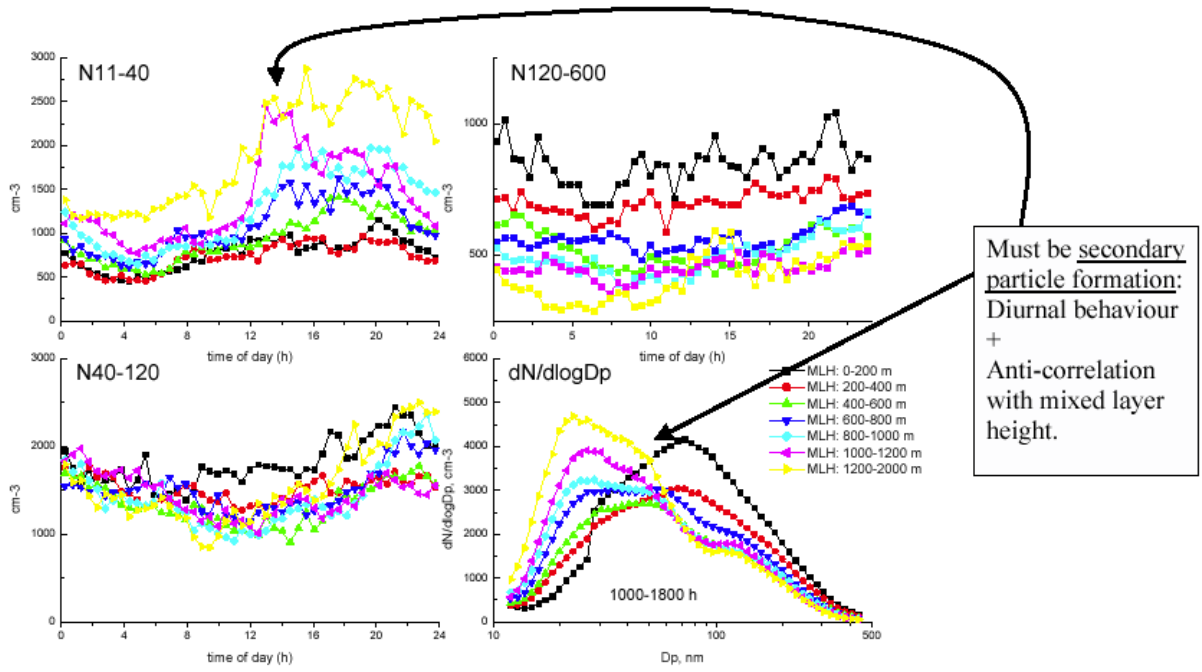


Figure 3.7 : Median particle number concentrations for different mixed layer heights (integrated counts for 11-40 nm, 40-120 nm and 120-450 nm ranges and particle number size distribution). From Wolfram Birmili.

3.2.5 Conclusions

- $PM_{2.5}$ and the numbers of particles above 30 nm are significantly reduced by increasing wind speed, an unstable atmosphere and a deep atmospheric boundary layer. There is no influence of temperature, relative humidity or of global irradiation amount (total cloud amount) on these particles.

- PM_{coarse} and particles below 30 nm behave differently. That is in agreement with their possible different pathways of production.
  - Dry, warm and sunny weather strongly favours PM_{coarse} concentrations which are unaffected by the wind speed. This is in agreement with PM_{coarse} (or a part of it) arising from resuspension processes.
  - Particles below 30 nm are also favoured by dry, warm and sunny weather (higher global irradiation amount), are unaffected by the wind speed and their numbers favoured by a well mixed atmospheric boundary layer. This suggests that at least a part of them is photochemically produced.

3.3 Overview of Possible Influential Sources

3.3.1 *Examination of wind directions*

Annex 2 presents the directions and distances of the nearest villages, roads and a description of Didcot Power Stations A and B. The sampling site is located in the SE part of the Research Centre.

Figure 3.8 presents the directions of some local, mesoscale (England) and regional (overseas) "sources". Actually, directions of cities/notable towns and countries (as opposed to seas/oceans) are considered. The following charts do not present the strength of each "source" (nor their distance).

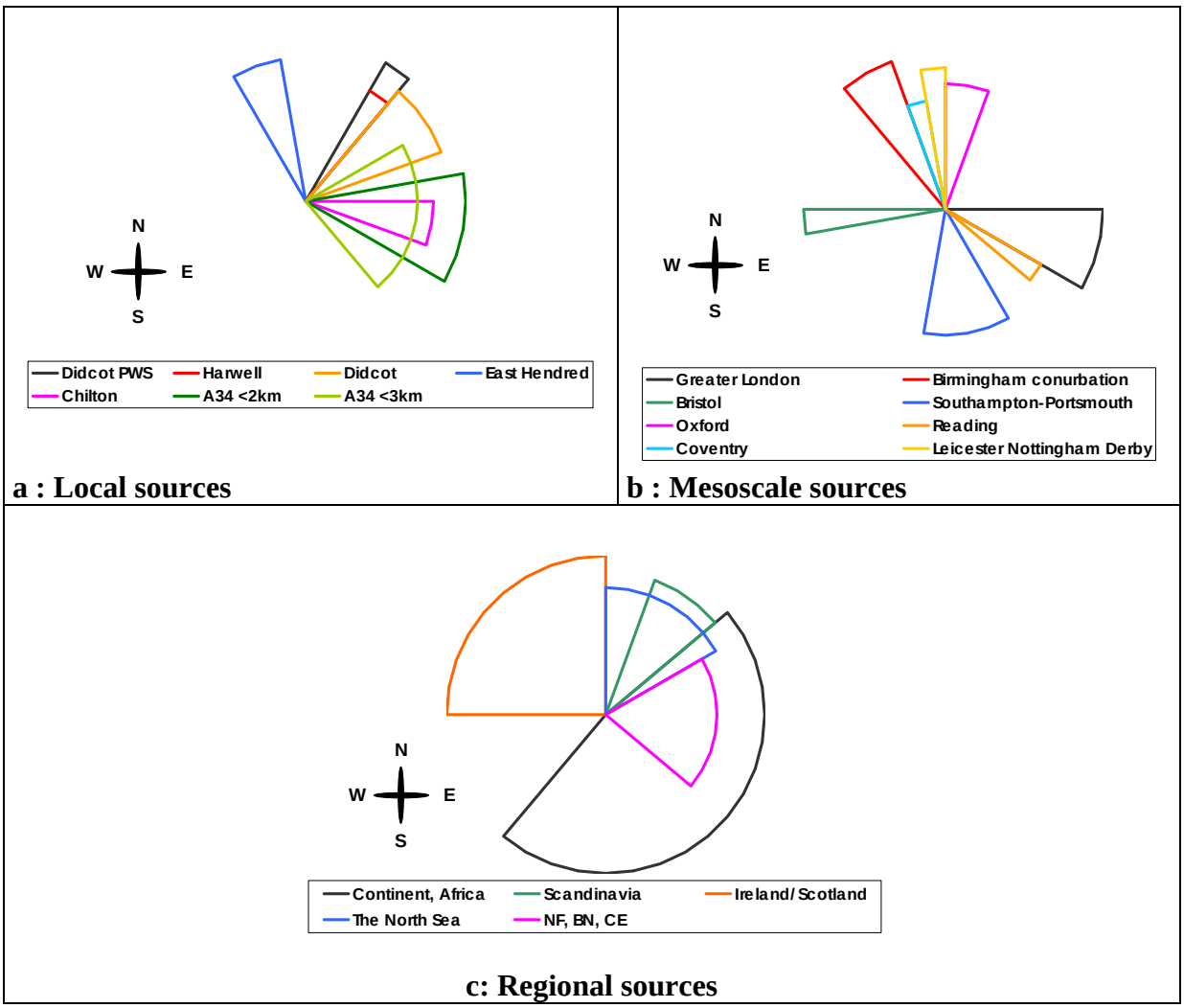


Figure 3.8: Main directions of (a) local sources, (b) mesoscale « sources », (c) regional « sources ». Didcot PWS is the local Power station ; NF, BN, CE=Northern France, Benelux, Central Europe

Figure 3.9 presents the percentiles of concentrations measured for each 10° wind direction bin and Figure 3.10 presents the median normalized concentrations for each 10° wind direction bin.

$PM_{2.5}$ and particle numbers ranging from 100 to 450 nm show higher concentrations when the wind blows from northerly and easterly directions; these are the directions of land/continents as opposed to seas/ocean and also the direction of the main local sources.

Particle numbers ranging from 30 to 100 nm show higher concentrations when the wind blows from easterly directions (80-120°). This pattern is associated with the directions of the main local sources (in particular the A34 highway). This is the particle metric that shows the smallest differences between the percentiles which would be in agreement with the possible influence of on-road emissions. Note that lower wind speed and sunnier weather are

associated with easterly air flows suggesting that anticyclonic conditions might also contribute to the higher concentrations measured (see Figure 3.11, later).

The pollution rose for PM_{coarse} is significantly different than the ones for $PM_{2.5}$ and particle numbers belonging to the accumulation mode. Very low PM_{coarse} concentration are measured when the wind blows from NW directions and very high concentrations are occasionally measured when the wind blows from NE directions (30-40° ; 80°) and south-west directions. The latter may be associated with marine aerosol.

The pollution roses for integrated particle numbers from 11 to 30 nm also show some peculiarities. Higher concentrations of 11-30 nm particles are measured when the wind blows from easterly, NW and SW directions. This implies that high PM_{coarse} concentrations and high integrated particle numbers from 11 to 30 nm may be associated with winds blowing from directions without any significant sources.

Much higher differences between percentiles can be seen for SO_2 and NO_x – especially for SO_2, the difference between the 25 and 75 percentiles is so high that only the 75 percentiles of concentration can be clearly seen on the chart and for legibility, median concentrations are presented in orange. Higher NO_x concentrations are measured when winds blow from SE and N directions ; but occasional much higher NO_x concentrations are measured when the wind blows from N directions (10°).

Concentrations of SO_2 below the detection limit of the monitor are often observed when the wind blows from westerly directions. Higher concentrations of SO_2 are measured when the wind blows from northerly directions (0-10°) and NE direction (40°). The source located at 40° (Didcot Power Station) leads to occasional very high concentrations (see 75 percentiles).

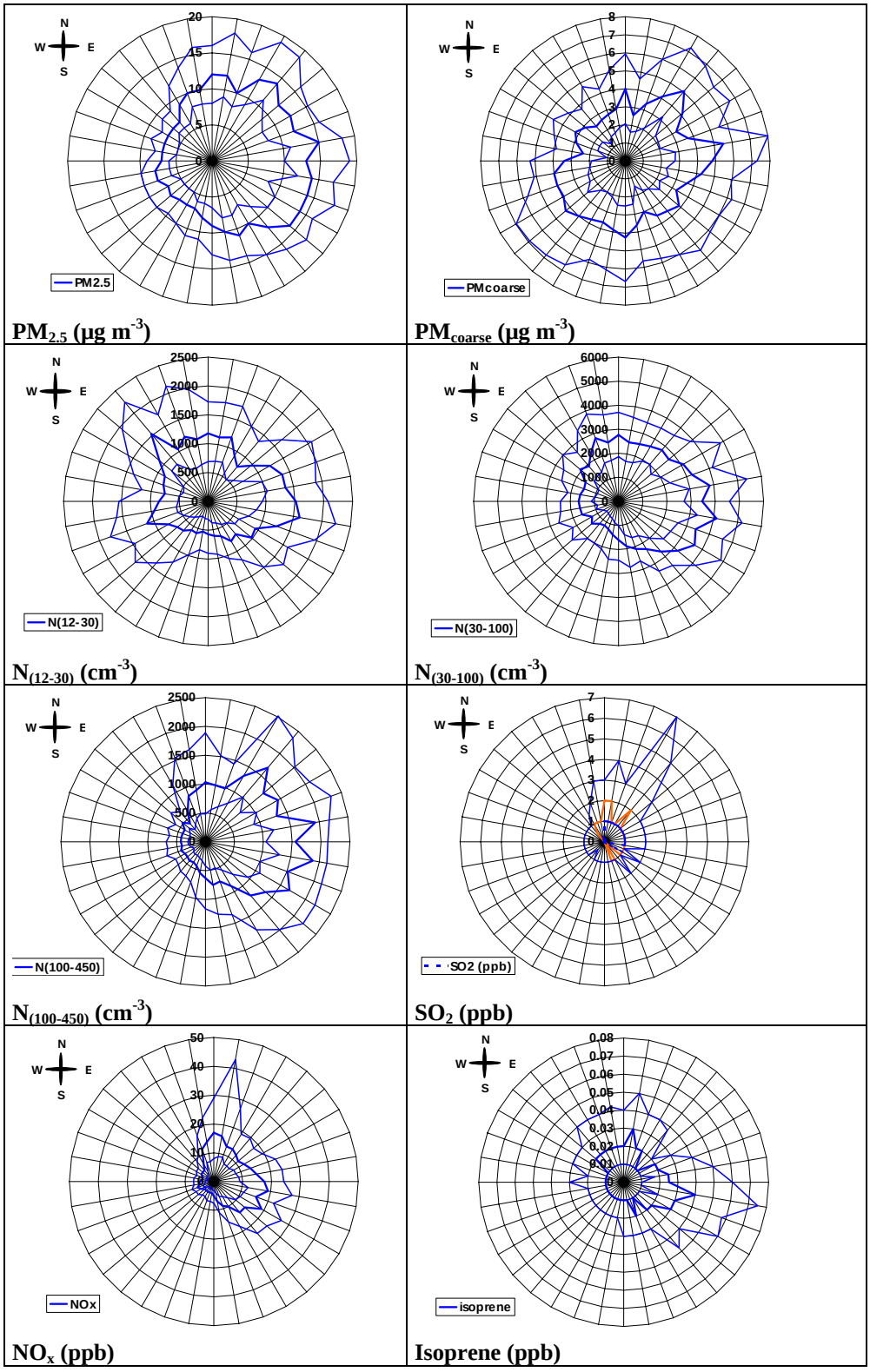
In contrast to the patterns observed for the particles, the patterns observed for SO_2 and NO_x suggest that a few local sources influence their concentrations.

Figure 3.10 presents the median normalized concentrations that inform the comparison between pollutants. A source (sources) that influence(s) particle numbers is observed in the SE direction (100-120°). The integrated numbers of particles above 30 nm are then very clearly associated with NO_x concentrations. This strong association suggests the possible influence of on-road emissions. Either on-road vehicle emissions from the local A34 highway

or vehicle emissions transported from the Greater London conurbation located in the same direction could explain these results.

In the 40° direction, the Didcot Power Station is clearly responsible for high concentrations of SO_2, accumulation mode particle numbers (100 to 450 nm), $PM_{2.5}$ and PM_{coarse} at Harwell.

An unknown source (sources) located in the 0-10° direction seem(s) to be responsible for high NO_x, SO_2 concentrations and possibly high $PM_{2.5}$ and PM_{coarse} concentrations at Harwell. Those high concentrations of NO_x are not associated with high concentrations of particle numbers, suggesting that this source is possibly not road traffic emissions.



$PM_{2.5}$ (µg m^{-3}) **PM_{coarse} (µg m^{-3})**

$N_{(12-30)}$ (cm^{-3}) **$N_{(30-100)}$ (cm^{-3})**

$N_{(100-450)}$ (cm^{-3}) **SO_2 (ppb)**

NO_x (ppb) **Isoprene (ppb)**

Figure 3.9 : Medians, 25 and 75 percentiles of different particle metrics and gas concentrations measured at Harwell per 10° wind direction bin.

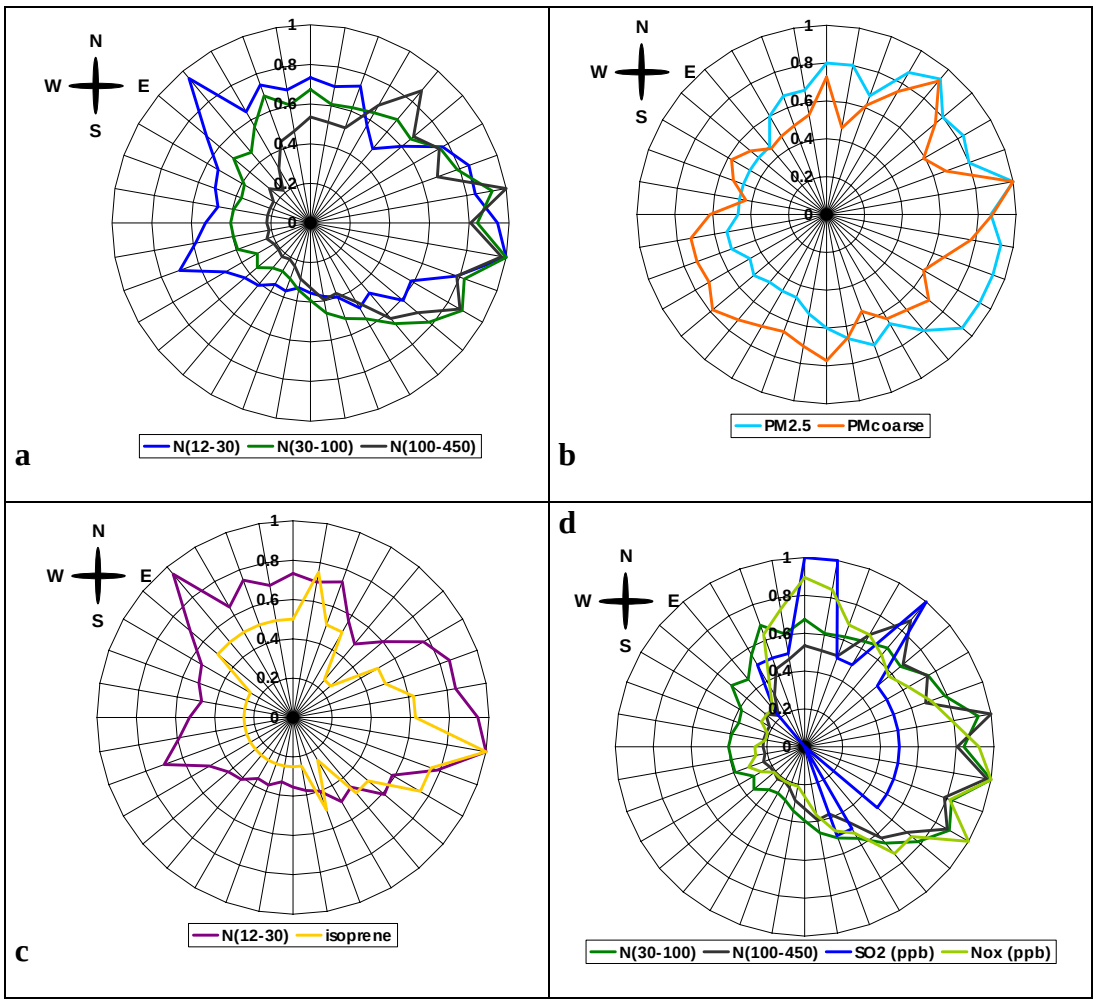


Figure 3.10: Normalised median concentrations per 10° direction bin
(Normalised conc.=conc./max conc.)

3.3.2 *Correlation matrix (interim results, only 2000 data)*

Table 3.2 presents the Spearman Rank correlation coefficients. The correlation coefficients above 0.45 (r^2>20%) are highlighted. Rank correlations gives a "measure" of the relationship between two datasets without assuming that they are related by a linear relation.

	N 11-30	N 30-100	N 100-450	O_3	SO_2	NO_x	Isoprene	WS	TCA	TEMP	RH(%)	RAIN
N(11-30)												
N(30-100)	0.55											
N(100-450)	0.18	0.76										
Ozone	0.00	-0.26	-0.18									
SO_2	0.27	0.55	0.61	-0.18								
NO_x	0.33	0.63	0.70	-0.48	0.62							
ISOPRENE	0.30	0.41	0.42	-0.23	0.22	0.37						
WS	-0.04	-0.30	-0.26	0.30	-0.13	-0.23	-0.23					
TCA	-0.16	-0.23	-0.17	-0.07	-0.10	0.00	-0.09	0.16				
TEMP	0.10	0.03	0.12	0.33	-0.08	-0.19	0.41	0.04	0.02			
RH(%)	-0.34	0.00	0.03	-0.57	-0.09	0.14	-0.10	-0.24	0.16	-0.49		
RAIN_AMT	-0.04	-0.08	-0.10	0.03	-0.14	-0.04	-0.05	0.07	0.26	-0.04	0.22	
GLBL IRAD AMT	0.14	0.23	0.20	0.27	0.06	-0.02	0.23	-0.16	-0.34	0.52	-0.27	-0.15

Table 3.2: Spearman Rank correlation coefficient matrix. WS: wind speed ; TCA: Total cloud amount

The high correlations between particle numbers above 30 nm and NO_x and SO_2 are also in agreement with the influence of anthropogenic emissions including on-road traffic and the Didcot Power Station.

No strong correlation is found with particle numbers ranging from 11 to 30 nm (except with $N_{(30-100)}$ particles). However, statistically significant, but weak correlations are found between $N_{(11-30)}$ and NOx, isoprene and the relative humidity. Note that similar weak anti-correlations with relative humidity are found with O_3 and particle numbers ranging from 11 to 30 nm.

3.3.3 *Conclusions*

Harwell is a “receptor site” located in southern England. It is very close to densely populated areas and anthropogenic sources. As a consequence, anthropogenic sources from various directions influence the concentrations measured at Harwell.

Results suggest the influence of vehicle emissions when the wind blows from SE directions. It is not possible to distinguish between the contribution of the local A34 road and the contribution transported from London.

Didcot Power Station located 7 km away is clearly seen as a source of SO_2 and particle mass at Harwell.

High PM_{coarse} and particle numbers ranging from 11 to 30 nm are associated with winds blowing from "clean" directions (westerly directions). This is possibly in agreement with non-anthropogenic sources for the PM_{coarse} or secondary sources for particle numbers ranging from 11 to 30 nm.

3.4 New Particle Formation at Harwell

3.4.1 *Assessment of the events of new particle formation at Harwell*

Three kinds of events are responsible for high particle numbers at Harwell.

(1) **Direct anthropogenic emissions**. High numbers of small particle are measured in vehicle exhaust emissions and in other combustion processes. In case of on-road emissions, high particle numbers are then associated with high NO_x concentrations (and high VOC concentrations).

(2) **Small scale nucleation events**. A small-scale nucleation event occurs in a small domain in the atmosphere (a few kilometres) where the conditions for nucleation are favourable. Contrary to the direct anthropogenic vehicle emissions, whose particles are formed in the exhaust of the tailpipe and dispersed afterwards, these particles would be photochemically produced in an already dispersed small plume of a few kilometres in size. A SO_2-rich plume from a power station, where SO_2 is photochemically oxidised during its atmospheric dilution, leading to high numbers of particles, is a first example of a small-scale nucleation event. Small scale nucleation events could also occur in a sunny region of the atmosphere, with cloud cover around; between two consecutive frontal passages; or in the outflow of clouds, where the particle condensation sink is very low. Coastal nucleation plumes saturated with low volatility oxidation products of halogens from seaweed, similarly to those observed at Mace Head, are a third example of small scale-nucleation events.

(3) **Large-scale nucleation events**. Large-scale nucleation events can be characterised by horizontal dimensions of 20-200 km and sometimes more. The existence of such events has been demonstrated by simultaneous measurements of the nucleation mode particles at different places (e.g. at Melpitz/Leipzig in Germany and Värriö/Hyytiälä/Tahkuse in

Finland). The continuous smooth evolution of the ultrafine particle size distributions over many hours is an indication of such events.

In practice, the border between the large-scale and small-scale nucleation events may be indistinct and criteria can be used to separate them.

The following criteria are used to extract the large-scale events of new particle formation. Such definitions are necessary to properly separate the large-scale nucleation, small-scale nucleation events and events of high particle numbers from anthropogenic emissions.

(1) Concentrations of [11-30 nm] particles above 8,000 cm^{-3} (1^{st} set); above 4,000 cm^{-3} (2^{nd} set).
(2) 60% of particle numbers below 30 nm
(3) Nucleation modes below 25 nm
(4) Episodes last more (or equal to) than 4 hours
(5) Episodes occurs mostly around or after midday.
(6) No correlation with NO_x (or 1,3 butadiene when no NO_x data are available)

Table 3.3 lists the events for the 3 years studied. Very few nucleation events occur at Harwell in comparison to other locations. Events occur from April to September (summer period).

1999 events	2000 events	2001 events
		April 15
		April 28
May 19	May 21	April 29
June 4	May 22	May 18
June 28	May 25	May 29
August 5	May 28	May 31
September 7	June 6	June 1
September 9	June 11	June 7
September 26	June 18	June 30
	July 31	August 31
		September 10
		September 15

Table 3.3: Events of nucleation with $N_{[11-30]}$ particles above 4,000 cm^{-3}; in blue those with $N_{[11-30]}$ particles above 8,000 cm^{-3}

3.4.2 *Average conditions of possible events of nucleation*

One episode, occurring on 19^{th} May 1999 is significantly different than the other ones. On 19^{th} May 1999, winds blew from N-NE directions (that is Didcot Power Station direction) and

particle numbers were clearly associated with very high SO_2 concentrations. It is highly possible that nucleation occurred in the plume of Didcot Power Station. New particle formation has been observed in the plumes of coal-fired power plants in the U.S. by Brock et al. (2002). This event has been removed in the calculation of the medians in Table 3.4. Few other events of high concentrations of small particles associated with very high SO_2 concentrations (and NE winds) were observed but were not considered further because they were short-lived episodes (less than 4 hours). Everything suggest that these events were events of new particle formation in the SO_2-rich plumes from Didcot Power Station.

Median concentrations and median meteorological parameters measured when a nucleation event was observed at Harwell are compared with median concentrations and median meteorological parameters measured during the midday period and median concentrations and median meteorological parameters measured during the midday period when winds blew from westerly directions (see later, except on 19th May 1999, nucleation events were observed at Harwell when the wind blew from westerly directions). Results are presented in Table 3.4.

The comparison between westerly air masses and episodes of nucleation shows that air masses were "cleaner" on days of nucleation : $N_{[100-450]}$ was on average about 20% lower and NO_x on average 25% lower on days of nucleation. Stronger differences are found for some meteorological parameters. The weather was less cloudy, warmer, dryer, a little bit more windy days of nucleation. The solar radiation was much stronger when nucleation events were observed.

Larger bursts (> 8,000 cm^{-3}) occurred on days of stronger solar radiation than nucleation events with particle numbers below 8,000 cm^{-3}.

Similar to Harwell, at Melpitz, days of nucleation events were days with high solar radiation, low cloud cover and stronger wind speed (Birmili, 1999). However, the particle surface area at Melpitz was on average 25% higher on these days. This suggests possible different conditions of both gas precursor concentrations and PSA. Average PSA were higher at Melpitz, but also the SO_2 concentrations were significantly higher at Melpitz than at Harwell.

	PSA	11-30 nm	30-100 nm	100-450 nm	O_3	SO_2	NO_x	Wind speed	TCA	T	RH	GIA
Nucleation > 4,000 cm^{-3}	56.8	4668	1853	344	38.5	0	3	5.7	5: fair	16.0	54.6	17754
Nucleation > 8,000 cm^{-3}	58.7	6511	2239	337	36.5	0	3	5.7	5: fair	16.0	55.5	19616
Midday data	85.9	944	1770	628	31	1	6	4.6	7: cloudy	13.6	70.0	8698
Midday data, westerly air masses (210-320°)	59.5	896	1258	423	32	0	4	4.6	7: cloudy	13.8	67.8	9306

Table 3.4: Medians for nucleation events, for midday data and for midday data with westerly winds. Particle surface area (PSA) in $\mu m^2/cm^3$, integrated particle numbers for the 11-30, 30-100, 100-450 nm ranges in cm^{-3}; O_3, SO_2, and NO_x in ppb, wind speed in m s^{-1}, total cloud amount (TCA) in Oktas, T in °C, RH in %, Global Irradiation Amount (GIA) in kJ/m^2. For the SO_2, 0 is below the detection limit of the instrument

Figure 3.11 shows that westerly air masses are generally associated with very cloudy (TCA = 7) and windy conditions. On the contrary, easterly air masses are associated with sunny weather and low wind speed.

All westerly airmasses associated with fair and windy weather do not lead to high small particle concentrations that can be attributed to a large-scale nucleation event at Harwell. On the other hand, easterly airmasses associated with fair, warm and windy weather are never associated with a large-scale nucleation at Harwell.

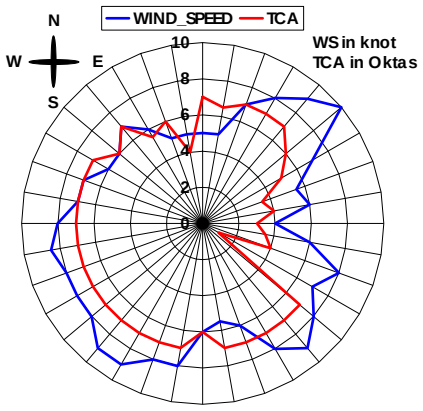


Fig 3.11. Median wind speed and TCA for 10° wind direction bins.

3.4.3 *Examination of air mass trajectories*

Backward air mass trajectories are plotted on the EMEP stereographic projection true at 60°N (Figures 3.12 and 3.13).

Except for two events of nucleation (and 19th May 1999), maritime air masses from the Northern Atlantic Ocean have reached Harwell. Before arriving at Harwell, the air masses have crossed rural areas of the UK: Cornwall and Wales.

The regional phenomenon of nucleation is necessary to observe the evolution of newly formed particles at a site. It is assumed to take place over a few hundred kilometres according to Kulmala et al. (2004). This regional phenomenon has a low probability at Harwell as it is close to many big cities (Bristol, Birmingham, London about 100 km away) and towns. A small change of wind direction could lead to different influences affecting Harwell.

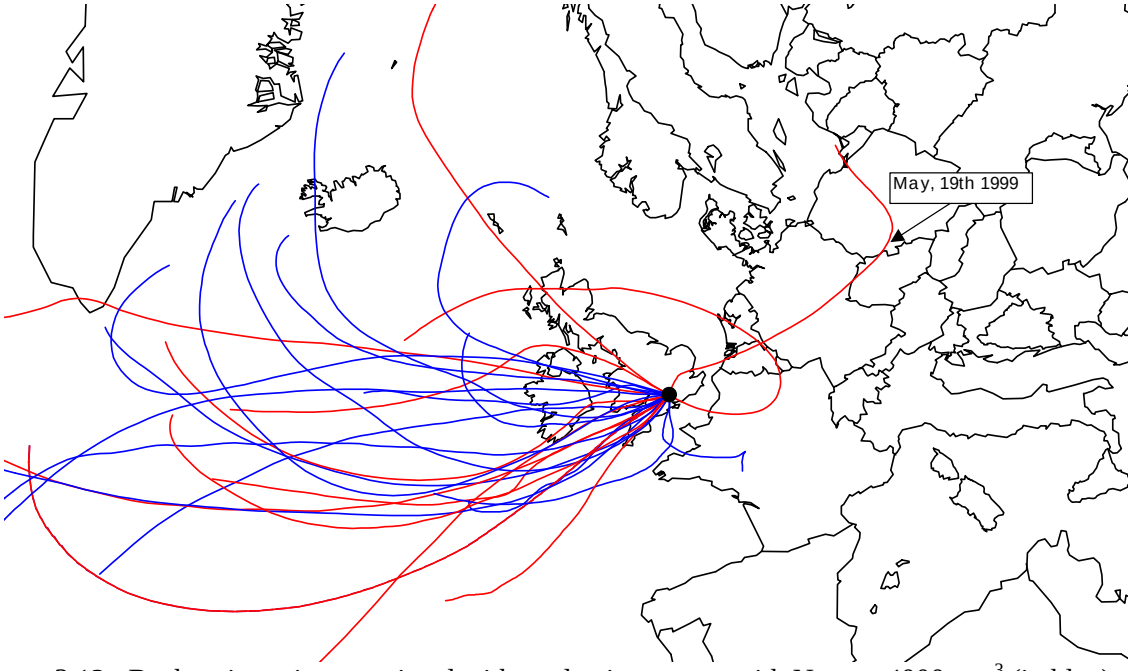


Figure 3.12 : Back trajectories associated with nucleation events with $N_{[11\text{-}30]}$>4000 cm^{-3} (in blue) and with $N_{[11\text{-}30]}$>8000 cm^{-3} (in red).

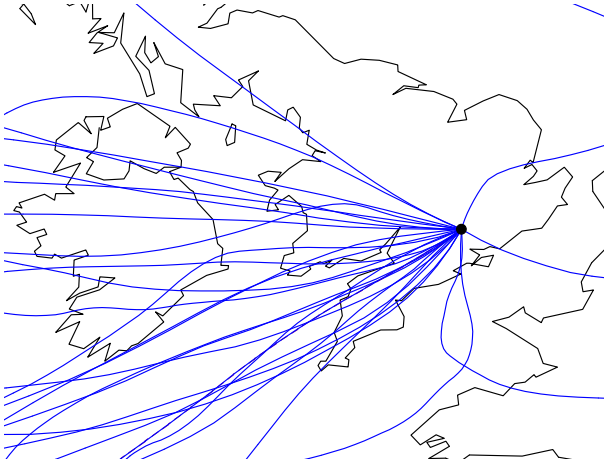


Figure 3.13 : Back trajectories associated with nucleation events.
Zoom on the UK

3.4.4 *Conditional probabilities to have a nucleation event at Harwell*

Nucleation episodes mostly occurred when the wind blew from westerly directions. Average conditions indicate that air masses were cleaner and the solar radiation higher. The following conditional probabilities to have a nucleation event at Harwell are computed and presented in Figure 3.14.

Conditional probabilities are far from 100% suggesting that westerly transport cannot entirely explain the nucleation events observed at Harwell. The highest conditional probabilities (reaching 20%) are found for WSW directions (Cornwall). This is also the direction of most of nucleation events with particle numbers above 8,000 cm^{-3}. A second main direction can be seen (NW, i.e. Wales) with conditional probabilities around 10%.

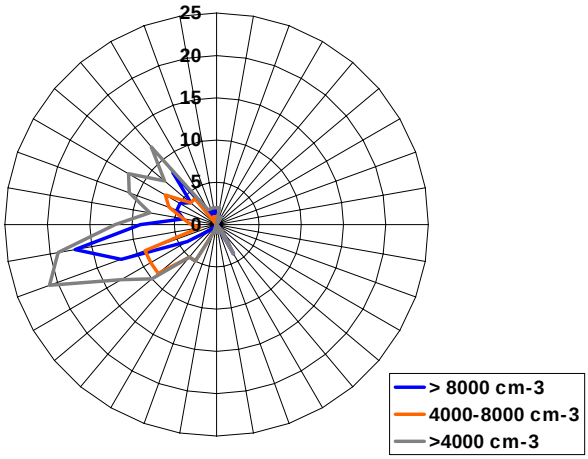


Figure 3.14: Conditional probabilities to observe a nucleation at Harwell (numbers > 4,000 cm^{-3}); to observe a nucleation event with numbers exceeding 8, 000 cm^{-3} and to observe a nucleation event with numbers ranging from 4,000 cm^{-3} to 8,000 cm^{-3}.

3.4.5 *Assessment of areas where nucleation has taken place*

The areas where new particle formation has taken place have been estimated (interim result: 2000 data only).

Nucleation particle modes at Harwell are often observed at sizes above 20 nm. At these sizes, particles may be a few hours old. It is assumed that newly formed particles have grown from about 1 nm. According to Kulmala et al. (2004), growth rates are between 1 and 20 nm/h for mid-latitudes. During summer periods growth rates mainly range from 4 to 10 nm/h (growth rates are considerably lower during winter periods) (Kulmala et al., 2004). Moreover, low rates are less probable for Harwell since they are observed in clean areas including clean polar areas unlike Harwell. Average growth rates at Harwell are assumed to be between 4 and 10 nm/h. The possible positions where nucleation had occurred are highlighted on the figures in red (from 4 to 10 nm/h) and in bold red (above 10 nm/h). On the chart, the length of the highlighted pathway also depends on the wind speed and on the modal diameters observed at Harwell.

The areas highlighted in Figure 3.15 are the areas located between the coast and Harwell. When growth rates above 4 nm/h are considered, results suggests that the nucleation has occurred when the maritime air masses have reached the coastal areas (except for the air masses that come from the continent that might be associated with a stronger growth rate because of higher concentrations of precursors).

Large-scale nucleation events observed at Harwell occur in clean westerly air masses. Results suggest that particular air mass types and weather situations favour nucleation. The following scenario is currently proposed. It will be confirmed extending the study to the examination of nucleation events that occurred in 1999 and in 2001. When cool and clean maritime air masses from the northern Atlantic ocean approach the warm land (days of new particle formation were warm and sunny), they become unstable and turbulent mixing sets in. As a consequence, anthropogenic and biogenic gases are well-mixed into that sunny atmosphere and they get oxidised over few hours. Their oxidation is followed by nucleation and new particle formation. The mixing of two air parcels with different temperature and different relative humidities has been shown to increase significantly the nucleation rates (Nilsson and Kulmala, 1998). Then, this situation would be highly favourable (strong mixing of air masses with different properties + very low pre existing particle surface area). Gaseous anthropogenic

emissions from the South Wales and Bristol areas might be entrained into those trajectories. Those newly-formed particles grow to larger sizes (30 nm maximum) during their transport to Harwell - located downwind - where “aged” particles are observed.

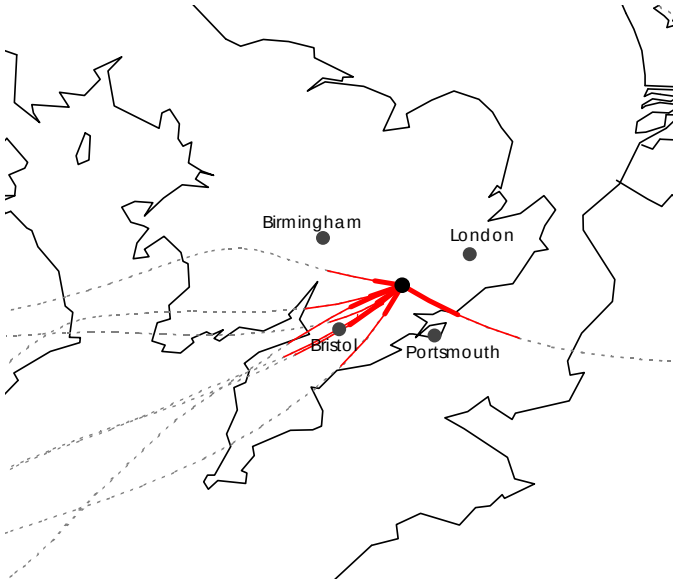


Figure 3.15: Possible positions where nucleation has occurred assuming a growth rate ranging from 4 to 10 nm/h (in red) and a growth rate above 10 nm/h (in bold red) – 2000 data only

3.4.6 *Conclusion*

Large scale new particle formation takes place predominantly in westerly cool and clean maritime air masses from the northern Atlantic ocean. When these cool air masses arrived at the western coast of the UK, conditions seem to be favourable for nucleation (turbulent mixing of air masses with different temperature and humidity, high solar radiation, a mix of biogenic and anthropogenic gases, low pre-existing surface area).

The combination of atmospheric variables (gases, local meteorology etc.) cannot wholly explain the nucleation events observed at Harwell. Nevertheless, it is clear that nucleation events occurred on warm days with high solar radiation and low pre-existing particle concentrations.

4. ACKNOWLEDGMENTS

To Andrew Allen for accurate location of the Harwell sampling site and regular site maintenance.

To Casella Stanger (Jeff Booker, Jon Alexander and David Harrison) for supplying the SMPS data.

To the British Atmospheric Data Centre (Annabelle Menochet) for supplying meteorological data and backwards trajectories.

To NILU (Finland) for supplying their stereographic projection of Europe.

5. REFERENCES

Birmili, W., 1999. Production of new ultrafine aerosol particles in Continental air masses, thesis, Leipzig univ., VWF Verlag fü Wissenschaft und Forschung GmbH, Berlin.

Birmili W., Stratmann, F., and Wiedensohler A., Covert D., Russel L. M., Berg O., 1997, Determination of differential mobility analyzer transfer functions using identical instruments in series. Aerosol Science and Technology 27, pp 215-223.

Birmili W. and Wiedensohler A., 2000. New particle formation in the continental boundary layer: meteorological and gas phase parameter influence. Geophysical Research Letters, vol. 27, pp 3325-3328

Birmili W. et al., 2000. Evolution of newly formed aerosol particles in the continental boundary layer : A case study including OH and H_2SO_4 measurements. Geophysical Research Letters, vol. 27, pp 2205-2208

Brock C.A., Washenfelder R. A., Trainer M., Ryerson T. B., Wilson J. C., Reeves J.M., Huey L. G., Holloway J. S., Parrish D. D., Hübler G., Fehsenfeld F. C., 2002, Particle growth in the plumes of coal-fired power plants, Journal of Geophysical Research, 107, D12, 2002.

Charron, A., Harrison, R. M., Moorcroft, S., Booker, J., 2004, Quantitative interpretation of divergence between PM_{10} and $PM_{2.5}$ mass measurement by TEOM and gravimetric (Partisol) instruments., Atmospheric Environment, 38, 415-423

Clayes M., Wang W., Ion A.C., Kourtchev I., Gelencsér A., Maenhaut W., 2004, Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide. Atmospheric Environment, 38, pp 4093-4098.

Easter, R.C. and Peters, L.K., 1994. Binary Homogeneous Nucleation: Temperature and Relative Humidity Fluctuations, Nonlinearity and Aspects of New Particle Production in the Atmosphere. Journal of Applied Meteorology 33, 775-784.

Harrison, R.M., Grenfell, J.L., Savage, N., Allen, A., Clemitshaw, K.C., Penkett, S., Hewitt, C.N. and Davison, B., 2000. Observations of New Particle Production in the Atmosphere of a Moderately Polluted Site in Eastern England. Journal of Geophysical Research 105, 17819-17832.

Kavouras, I.G., Mihalopoulos, N. and Stephanou, E.G., 1998. Formation of Atmospheric Particles from Organic Acids Produced by Forest. Nature 395, 683-686.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R. and Seinfeld, J.H., 1999. Ternary Nucleation of H_2SO_4, NH_3, and H_2O in the Atmosphere. Journal of Geophysical Research 104, 26349-26353.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso M., Lauri, A., Kerminen, V.-M., Birmili, W., McMurry, P. H., 2004, Formation and growth rates of ultrafine atmospheric particles: a review of observations. Journal of Aerosol Science 35, 143-176.

Nilsson, E.D., and Kulmala, M., 1998. The Potential for Atmospheric Mixing Processes to Enhance the Binary Nucleation Rate. Journal of Geophysical Research 103, 1381-1389.

O'Dowd, C.D., Aalto, P., Hameri, K., Kulmala, M. and Hoffmann, T., 2002. Atmospheric Particles from Organic Vapours. Nature 416, 497-498.

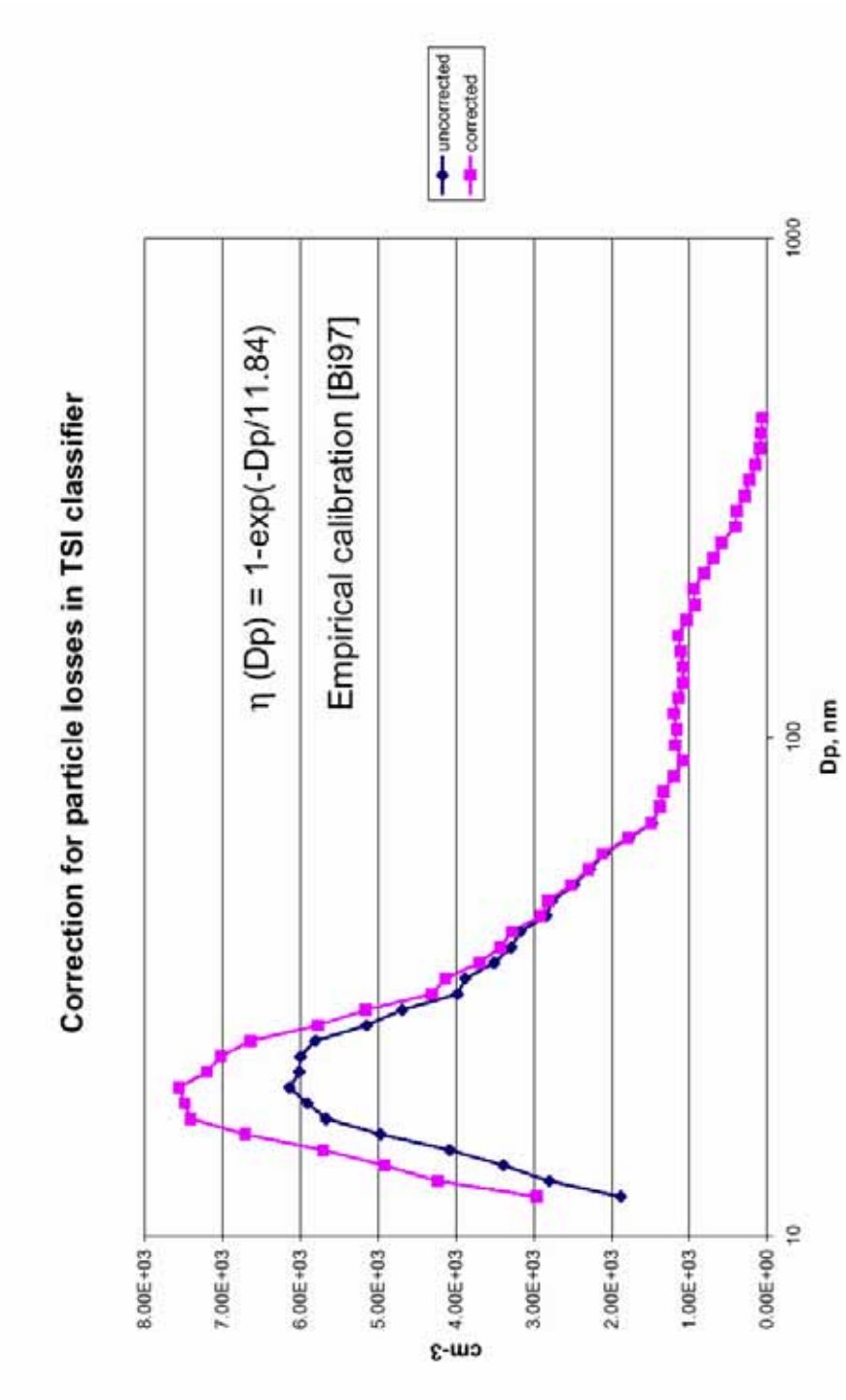
Raes F., Dingenen R. V., Vignati E., Wilson J. Putaud J.-P, John H. Seinfeld, Adams P., 2000, Formation and cycling of aerosols in the global troposphere., Atmos. Environ., 34, 4215-4220.

Väkeva, M., Hämeri, K., Puhakka, T., Nilsson, E. D., Hohti, H. and Mäkela, J. M., 2000, Effects of meteorological processes on aerosol particle size distribution in an urban background area., Journal of Geophysical Research 105, 9807-9821.

Wang, S.C., and Flagan, R.C., 1990. Scanning Electrical Mobility Spectrometer. Aerosol Science and Technology 13, 230-240.

Annex 1

Classifier Transfer Function used to correct SMPS data (Birmili et al., 1997)



Annex 2

Possible local sources of pollutants measured at Harwell

Didcot Power station

- first set of chimneys: 33-35°, 7.5 km away
- central chimney: 36°, 7.3 km away
- second set of chimney: 38-41°, 7 km away

Didcot A is a coal-fired power station with a capacity of 2,000 MW. Didcot A have the capability to burn gas on 3 of the 4 generating units. Didcot B is a 1,400 MW combined cycle gas turbine plant that burns natural gas.

Local villages

- Didcot town: 42-68°, 6 km away
- Harwell village: 33-42°, 3.5 km away
- East Hendred village: 335-350°, 2.5 km away
- Chilton village: 88-108°, 2 km away
- Upton, 78-83°, 4.5 km away
- Steventon: 357-8°, 5.5 km away
- Milton + Milton Park Estate: 15-27°, 6 km away
- Blewbury: 87-95° 6 km away
- Sutton Courtenay, 21-26°, 7.5 km away
- Drayton, 4-9°, 7.5 km away

Local significant road

- A34 road:
    - less than 2 km away: 84-122°
    - less than 3 km away: 62-137°
- A4185 road, less than 2 km away: 46-86°