Energy and Resources Research Institute

Faculty of Engineering

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Modal Analysis of Roadside Particle Size Distributions

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Introduction

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- UK air quality standards currently based on running 24 hour and annual means for mass based PM_{10} and $PM_{2.5}$.
- **Questions raised as to whether these metrics best represent exposure in terms harmful characteristics of particles.**
- Uf ≤100 nm in diameter only contribute 1-20 % of particle mass, but can represent >90 % of particle number concentrations (PNC) in diesel exhaust or at urban roadside.
- **If high numbers of Uf's contribute to inflammatory responses - are mass based standards are the optimal way to reduce impact of particles on health?**
- Additional use of a NC based emission standard outlined in proposals for Euro VI legislation for light duty vehicles (EC 715/2007).
- Surface area has also been identified as an important particle characteristic in toxicological experiments.

Implications for air quality measurements?

Inflammation in rat lungs as a function of particle surface area Brown *et al*. (2001)

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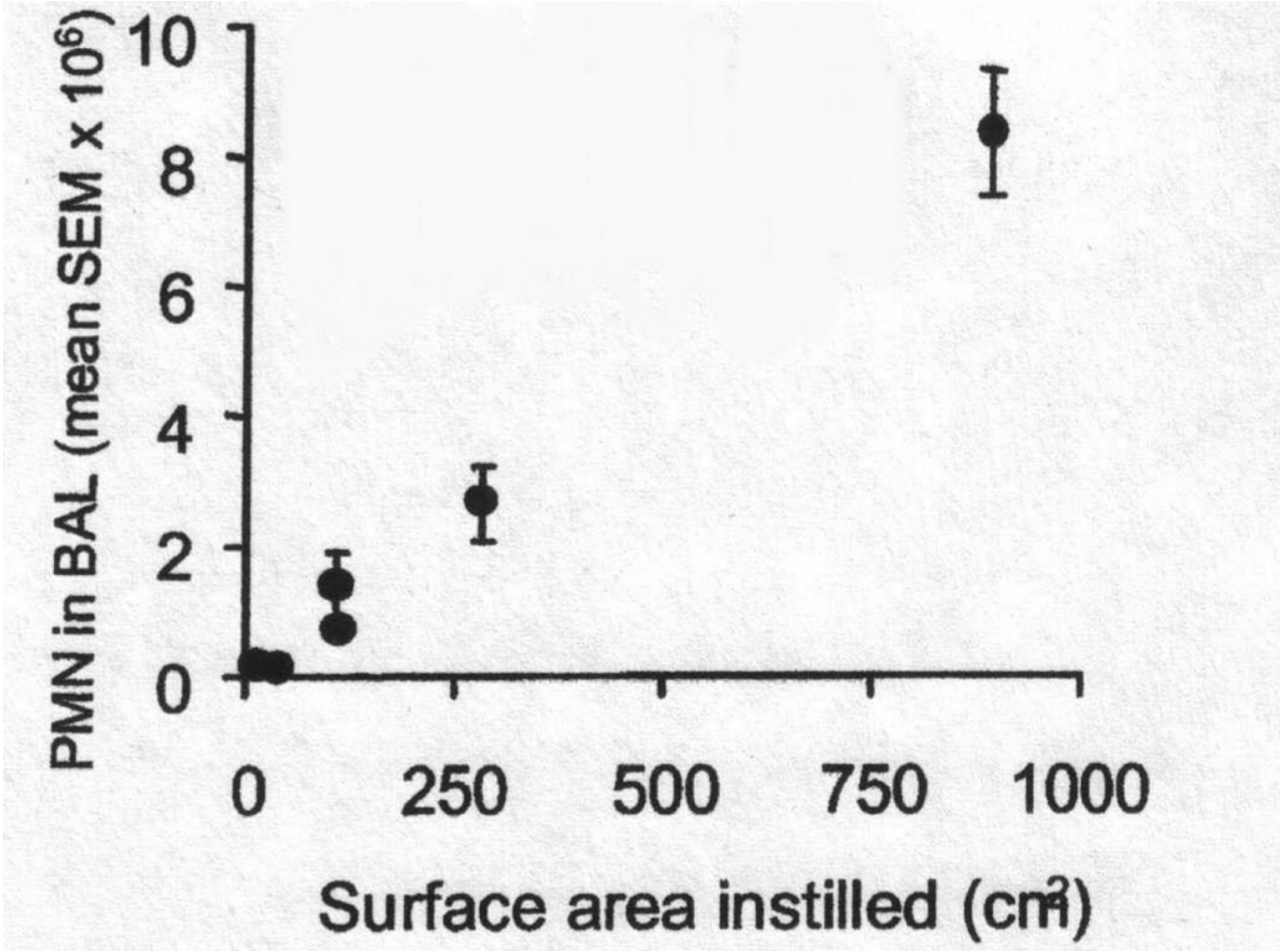

Comparison of number, surface area and volume distributions (Leicester roadside)

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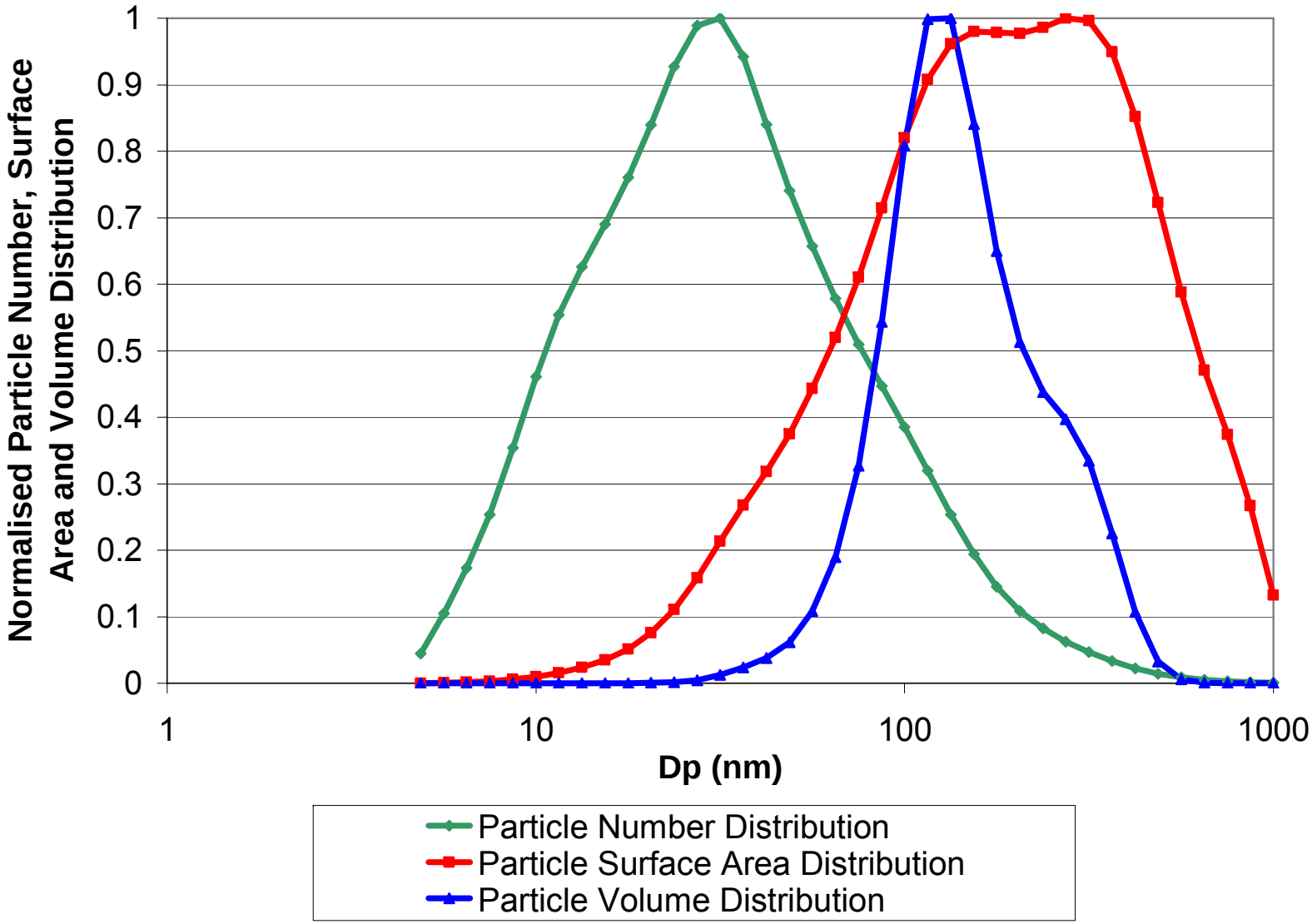

Particle Metrics

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- In terms of measurement mass and PNC easier to determine than full size distribution or surface area.
- Some studies report low correlations between total PNC and mass concentrations esp. at background sites.

  - Reducing particle surface area can lead to increases in PNC due to particle nucleation being favoured over condensation of semi-volatiles.

- Chemical complexity, daily, seasonal and spatial variability in composition within distribution is possible reason for lack of consensus.
- Both source characteristics and atmospheric processing have a role to play in determining the overall nature of the particle size distribution.
- Particle size distributions can therefore vary spatially and temporally within an urban area.
- Are there any general characteristics?
- Can we simplify descriptions of complex distributions e.g. through modal analysis?

Particle Mixing State – toxicological significance?

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Nucleation mode particles (≤10 nm):

Suggested to be predominantly liquid droplets composed of semi-volatiles from e.g. unburnt fuels, sulphates, nitrates or secondary organics.

Aitken mode particles (~30-100 nm):

Suggested to be internally mixed particles with a soot based core and condensed semi-volatiles.

Accumulation mode particles (~200-300 nm):

Suggested to be aged particles that have grown through atmospheric processing.

Coarse mode particles (>2 μm):

Mechanically generated such as wind blown dusts, break wear etc.

Euro VI PNC emissions limit suggests that measurements should be based on techniques that exclude the more volatile nucleation mode fraction.

Overall size distributions
PNC – modal fitting.

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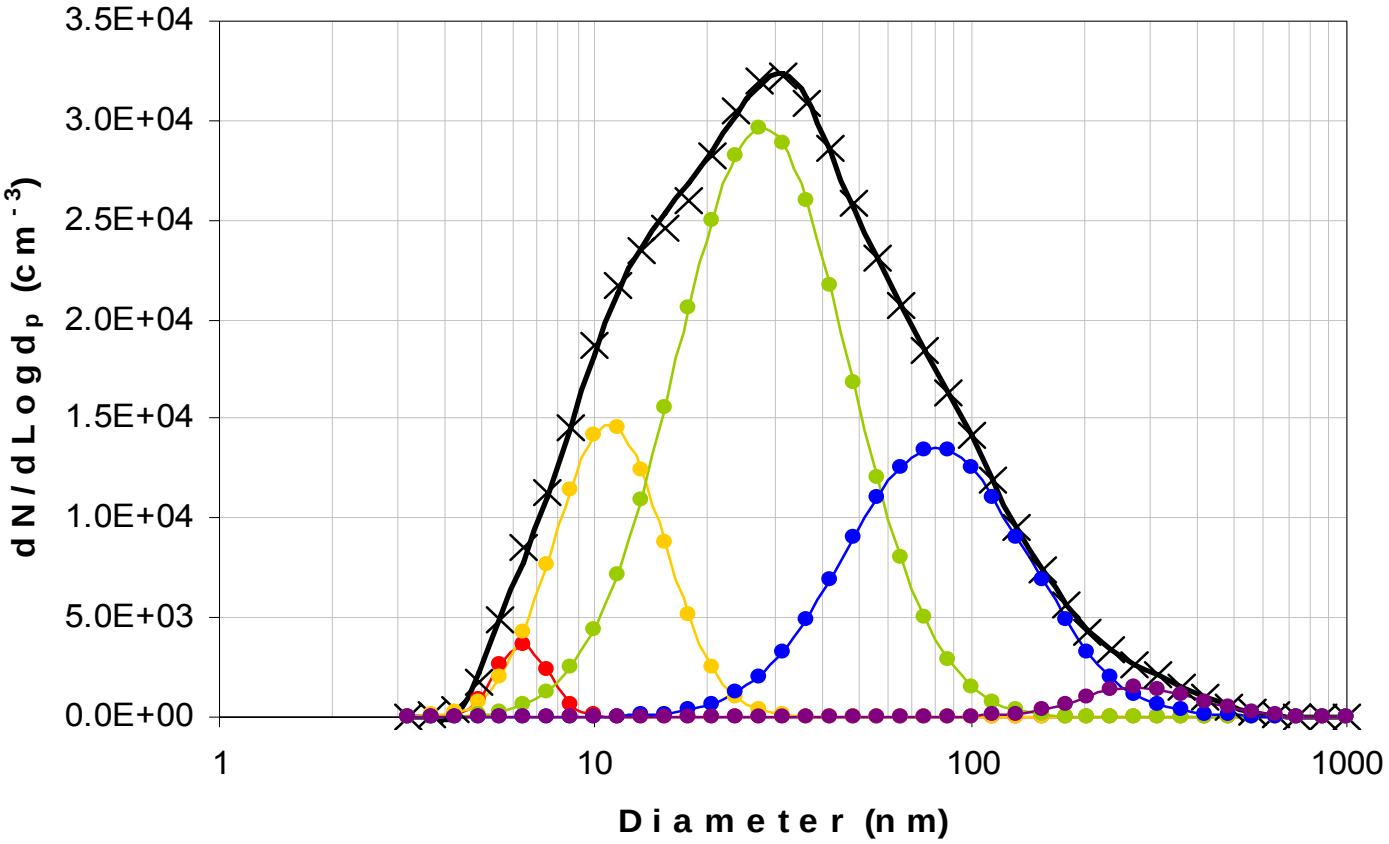
Modal fit reflects different sources and particle mixing and ageing.

$$\frac{dN_{TOTAL}}{dLog_{10}d_p} = \frac{dN_I}{dLog_{10}d_p} + \frac{dN_{II}}{dLog_{10}d_p} + \ldots + \frac{dN_n}{dLog_{10}d_p}$$



Mode 1 – Nucleation Short lifetime ~ 6nm

Mode 2 - Nucleation Short lifetime ~ 10nm

Mode 3 – Aitken ~ 30nm

Mode 4 – Aitken ~80nm

Mode 5 - Accumulation Aged and longer lived ~ 300nm

Relative importance of modes depends on emissions and atmospheric processing

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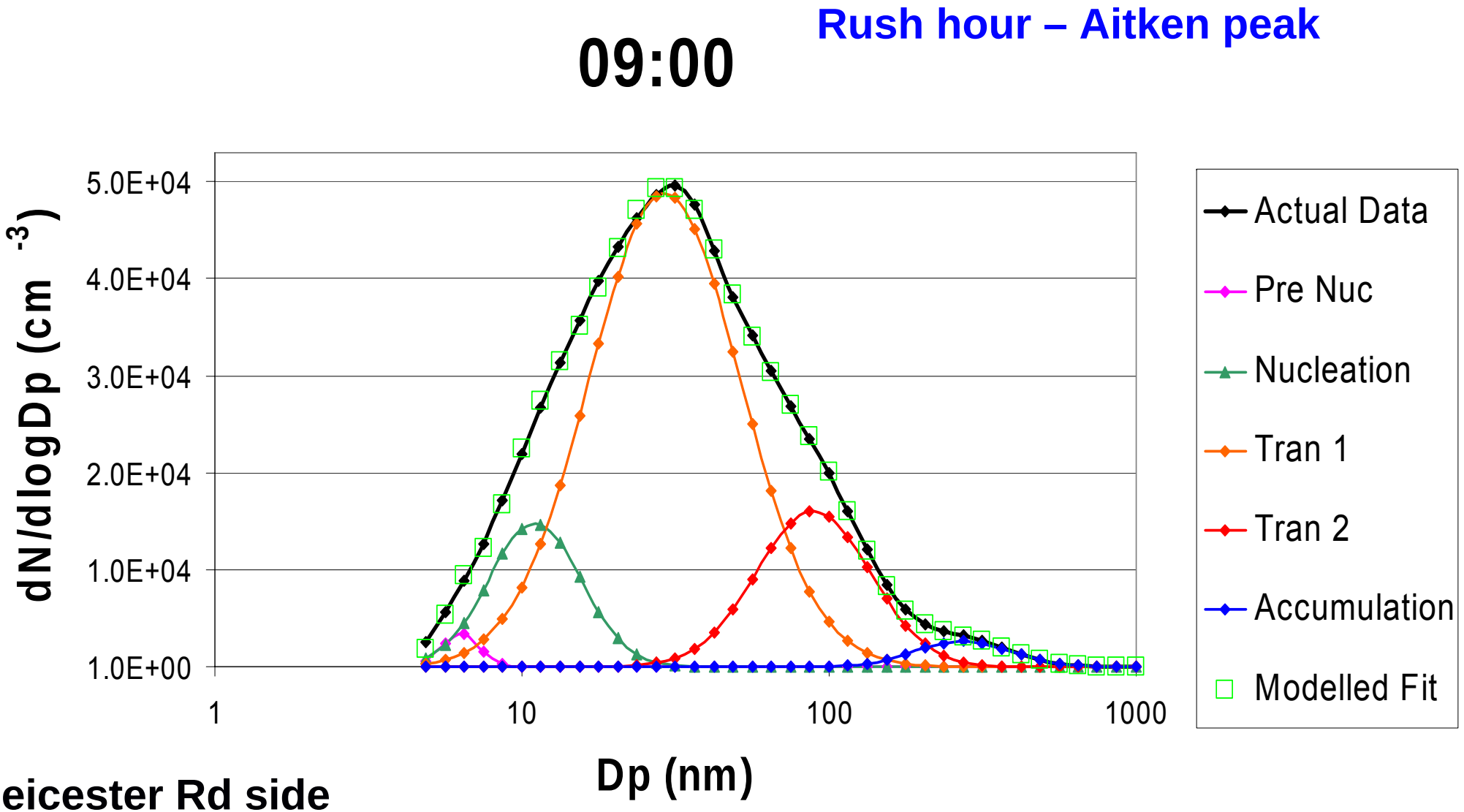
Rush hour – Aitken peak



Leicester Rd side

Afternoon – reduction in Aitken mode, relative increase in nucleation mode.

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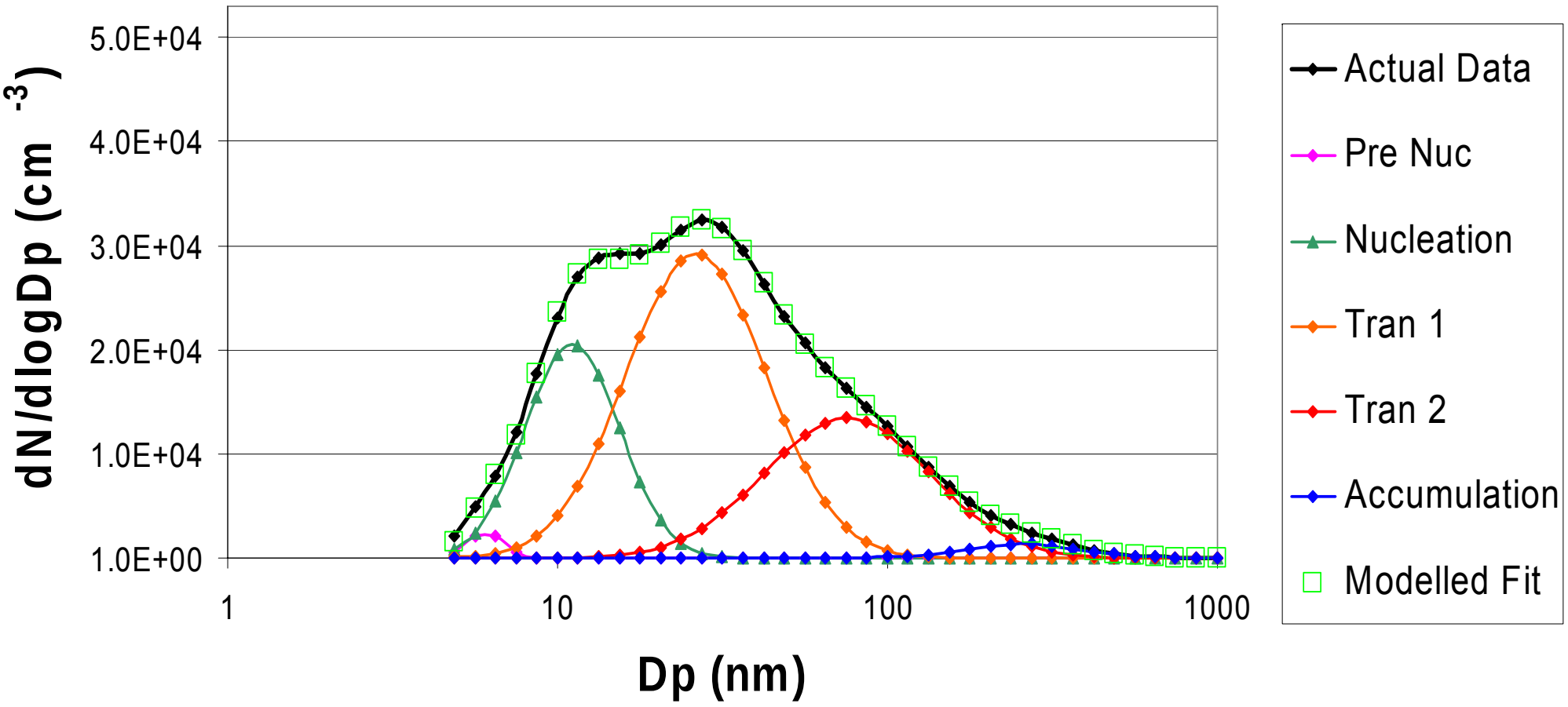
15:00



Relative increase in nucleation mode at night.

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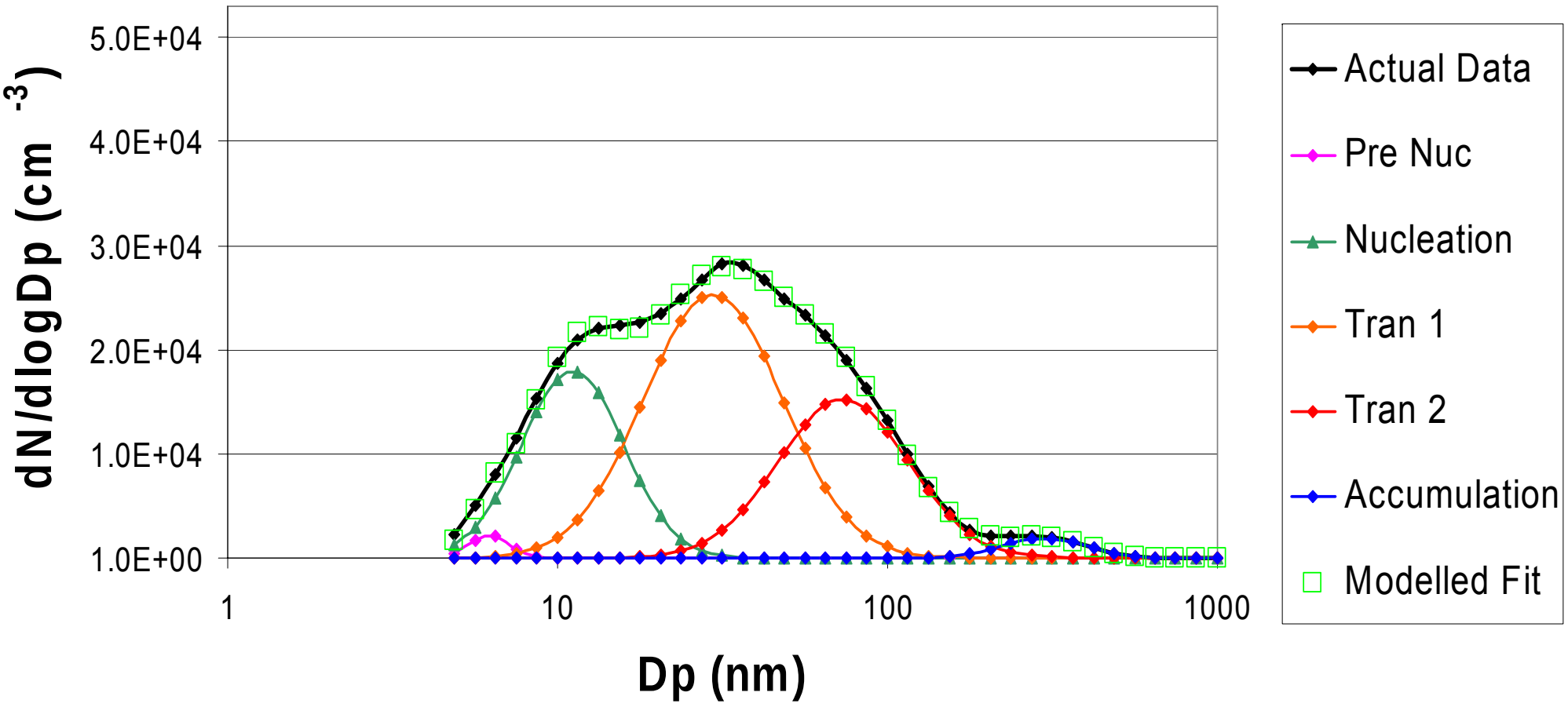
23:00



Fate of semi-volatiles

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- ***Volatility*** is a key characteristic and can affect measurement techniques as well as particle mixing state and toxicological effects.
- Volatile material can contribute to nucleation or Aitken/accumulation modes depending on dilution conditions.
- The **TEOM** has received attention since it heats sample to 50ºC to reduce effects of humidity causing potential loss of semi-volatile material.

  - Average correction factor does not take account of variability with location, season, time of day.

- However, PNC also affected by volatility and atmospheric dilution conditions which determine fate of semi-volatile material.

Relationship between nucleation mode and PNC

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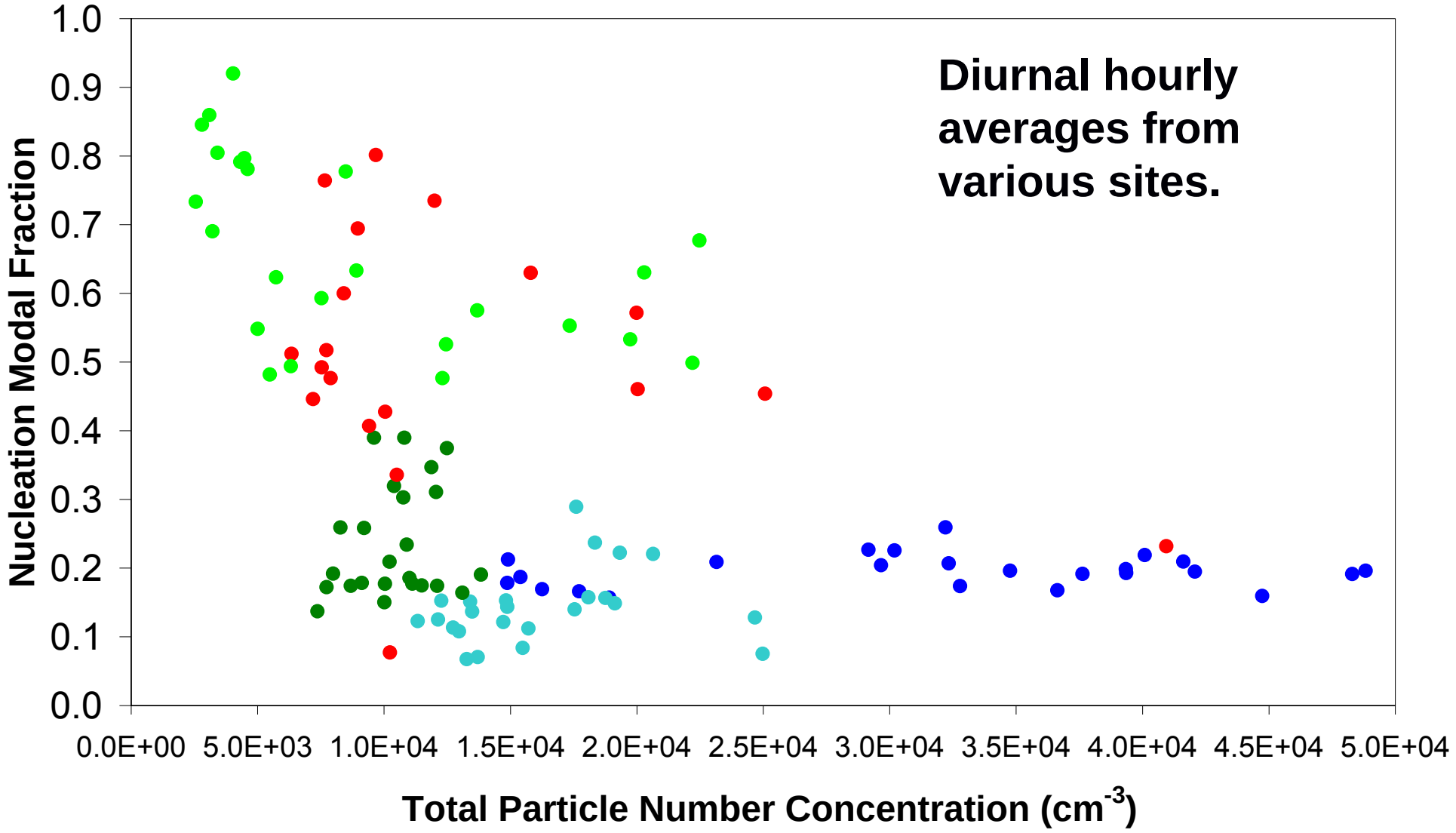

Relationship between nucleation mode and PNC

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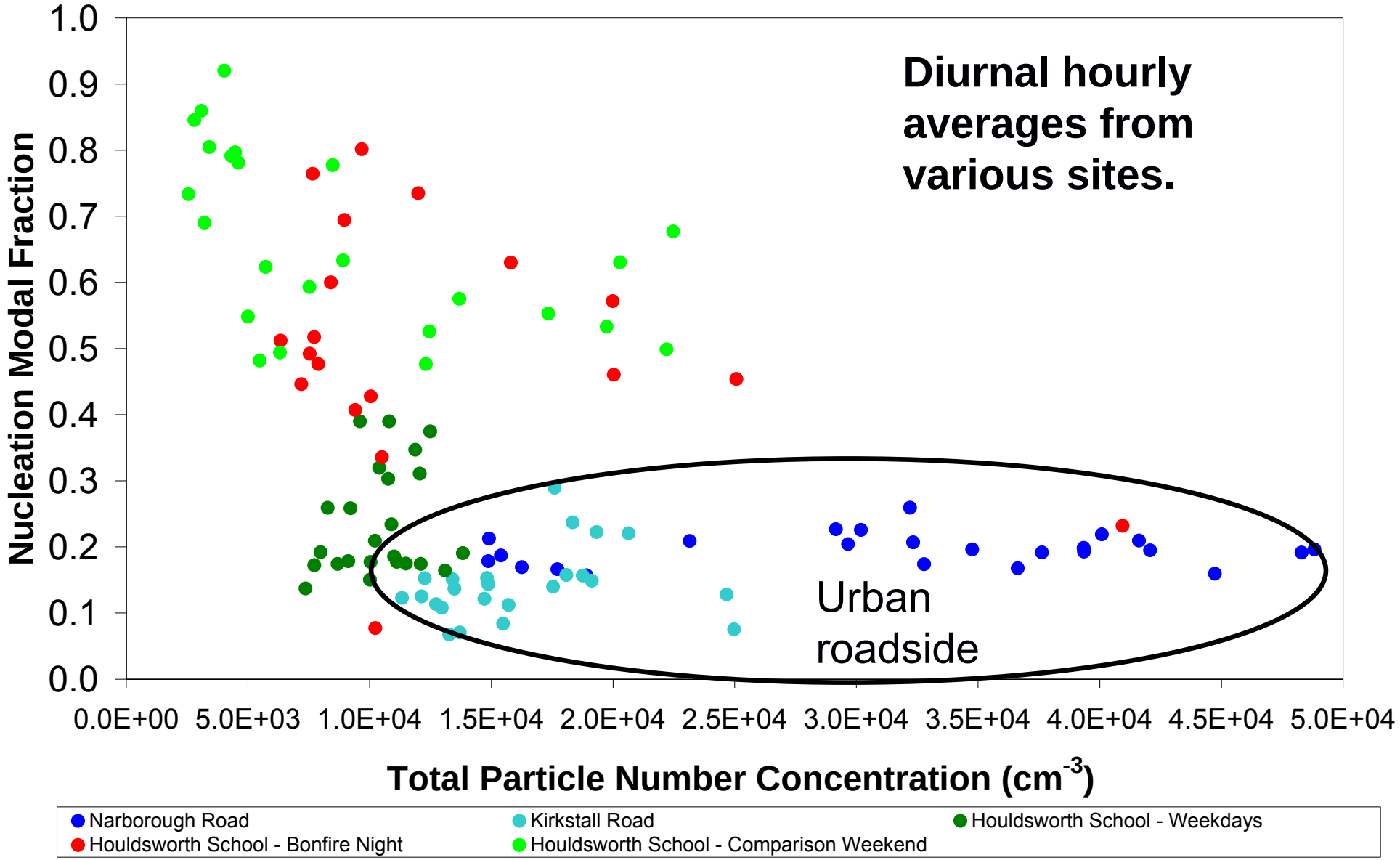

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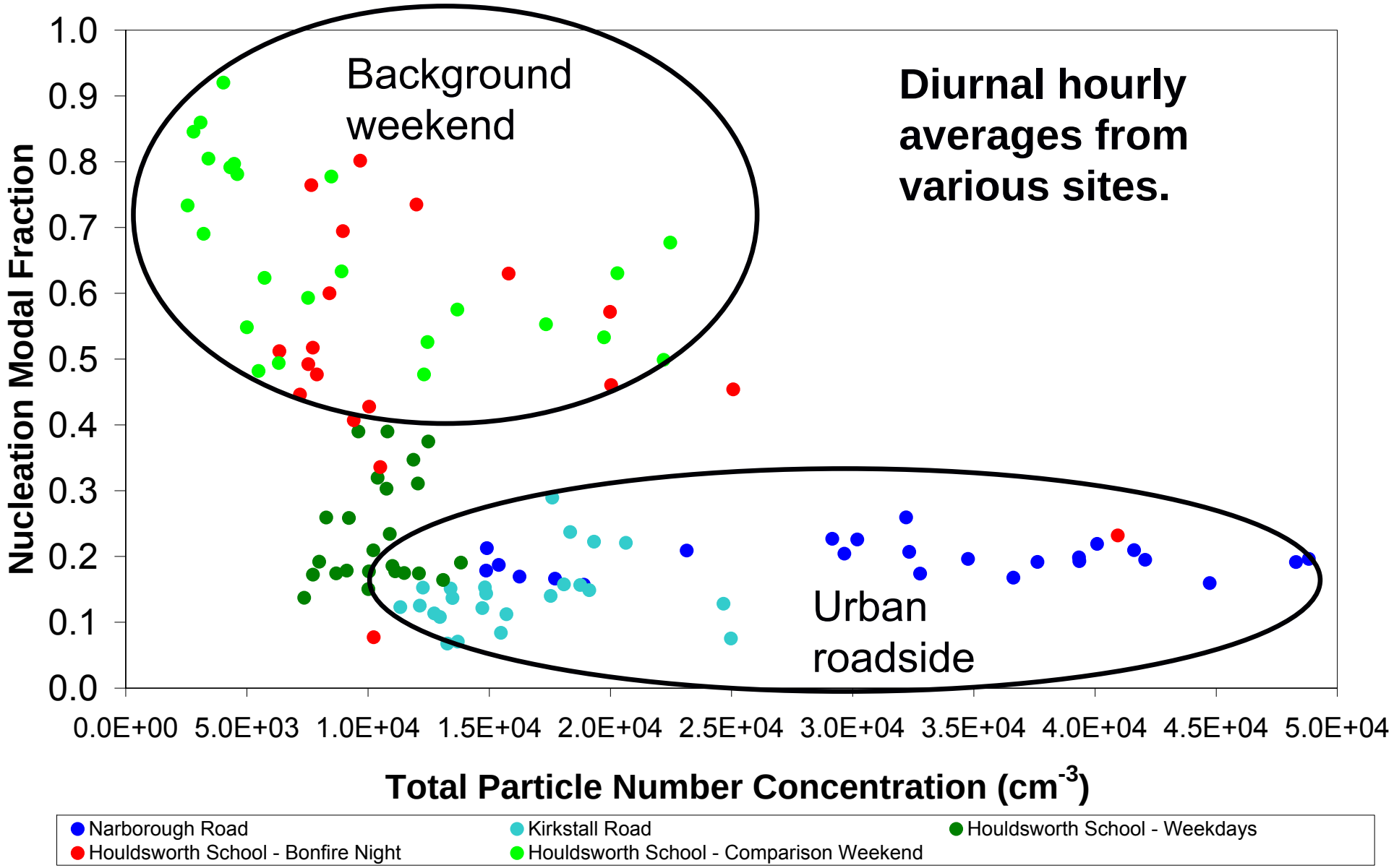

Relationship between nucleation mode and PNC

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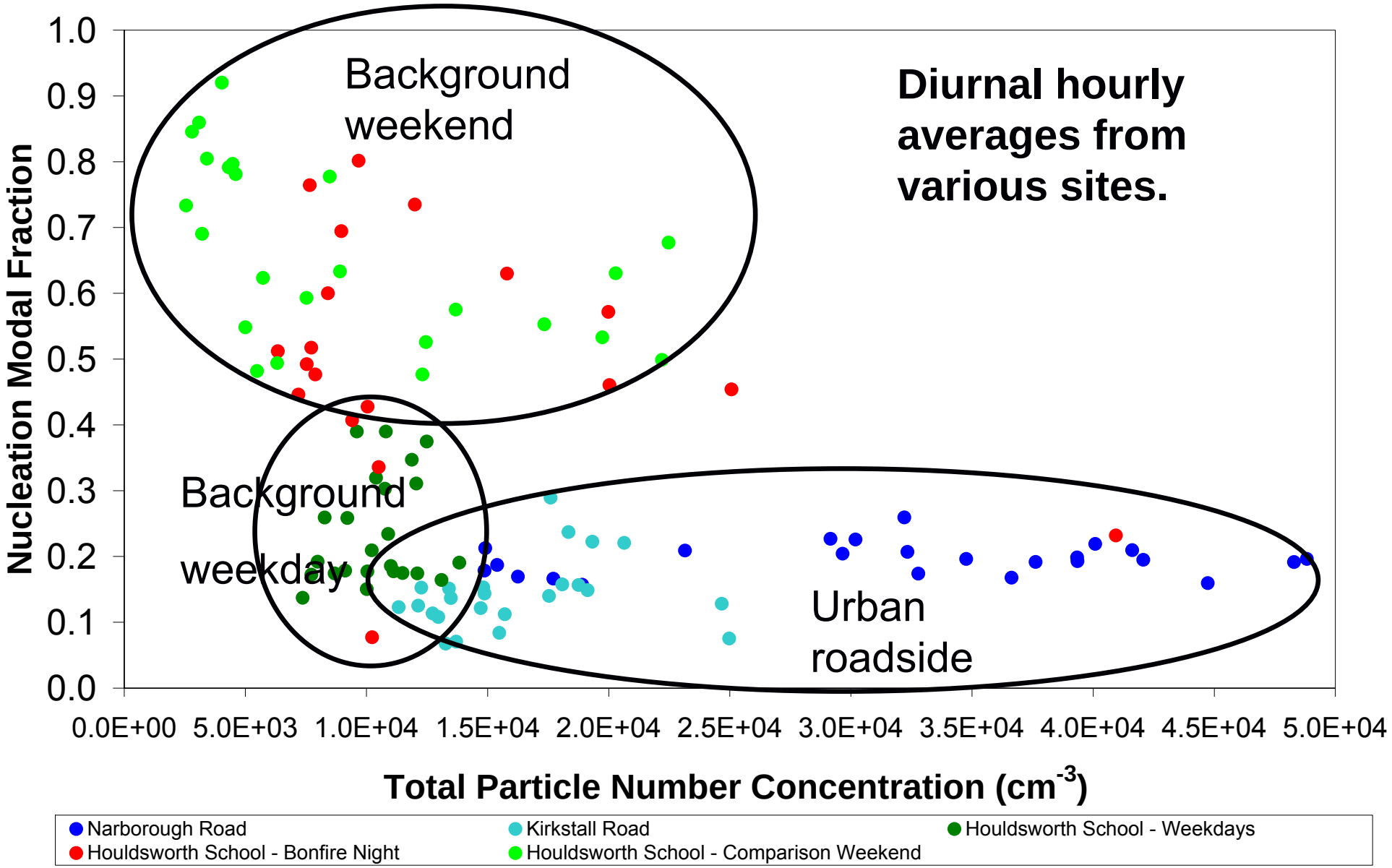

Effect of Local Wind Speed (Leicester)

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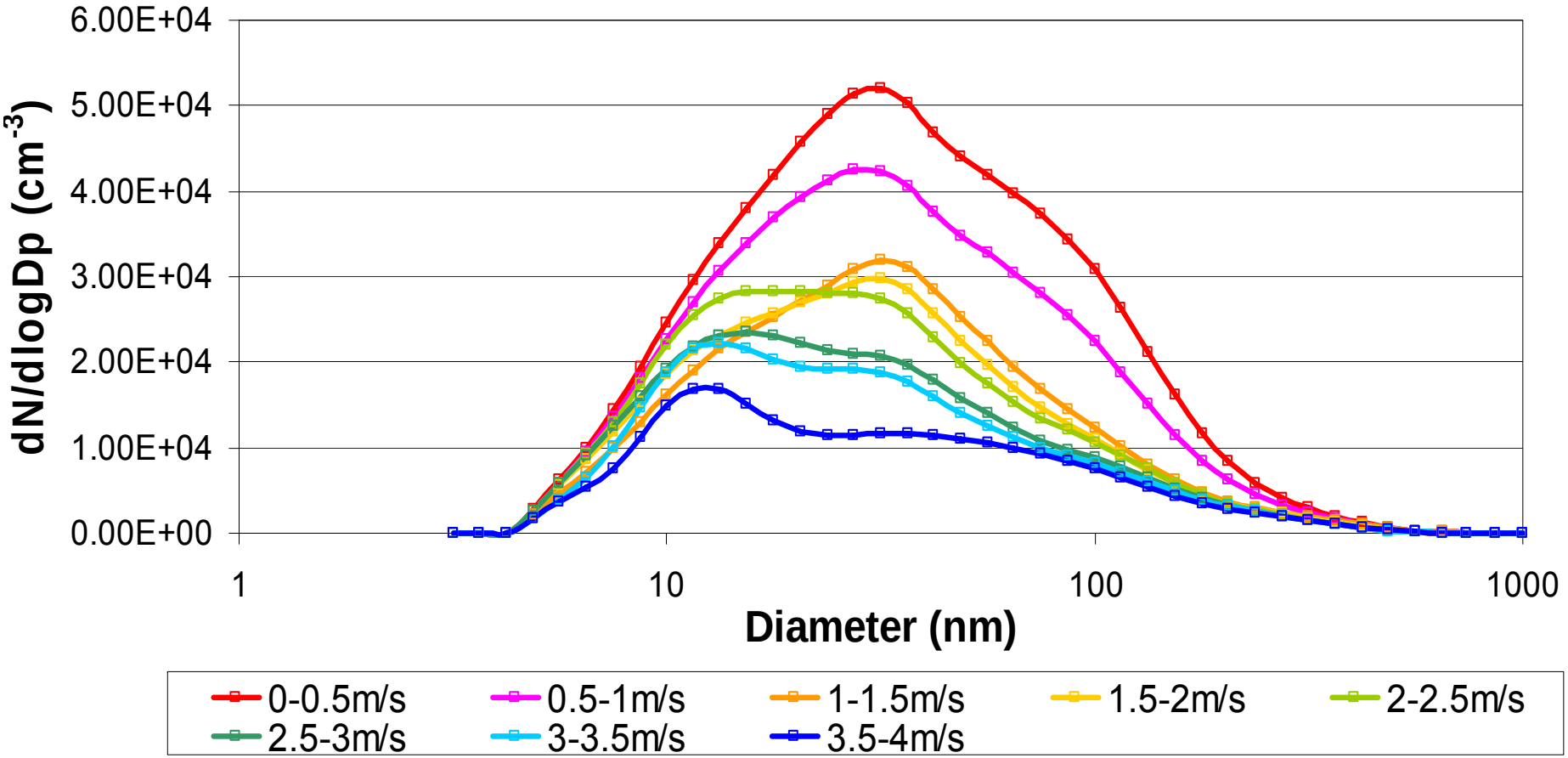
Increases in wind speed affect Aitken mode particles but less so nucleation mode.



Implications for PNC as a metric

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Decreases in Aitken and accumulation mode particles due to pollution control or effective dispersion could result in increases in nucleation particle numbers.

The toxicological significance of the nucleation mode is unclear at present.

Should they be counted as equally important to the other particle modes or should they be removed as suggested in the proposed Euro VI legislation?

Highly transient concentrations

(DMS, differential mobility spectrometer ~ 1 s resolution)

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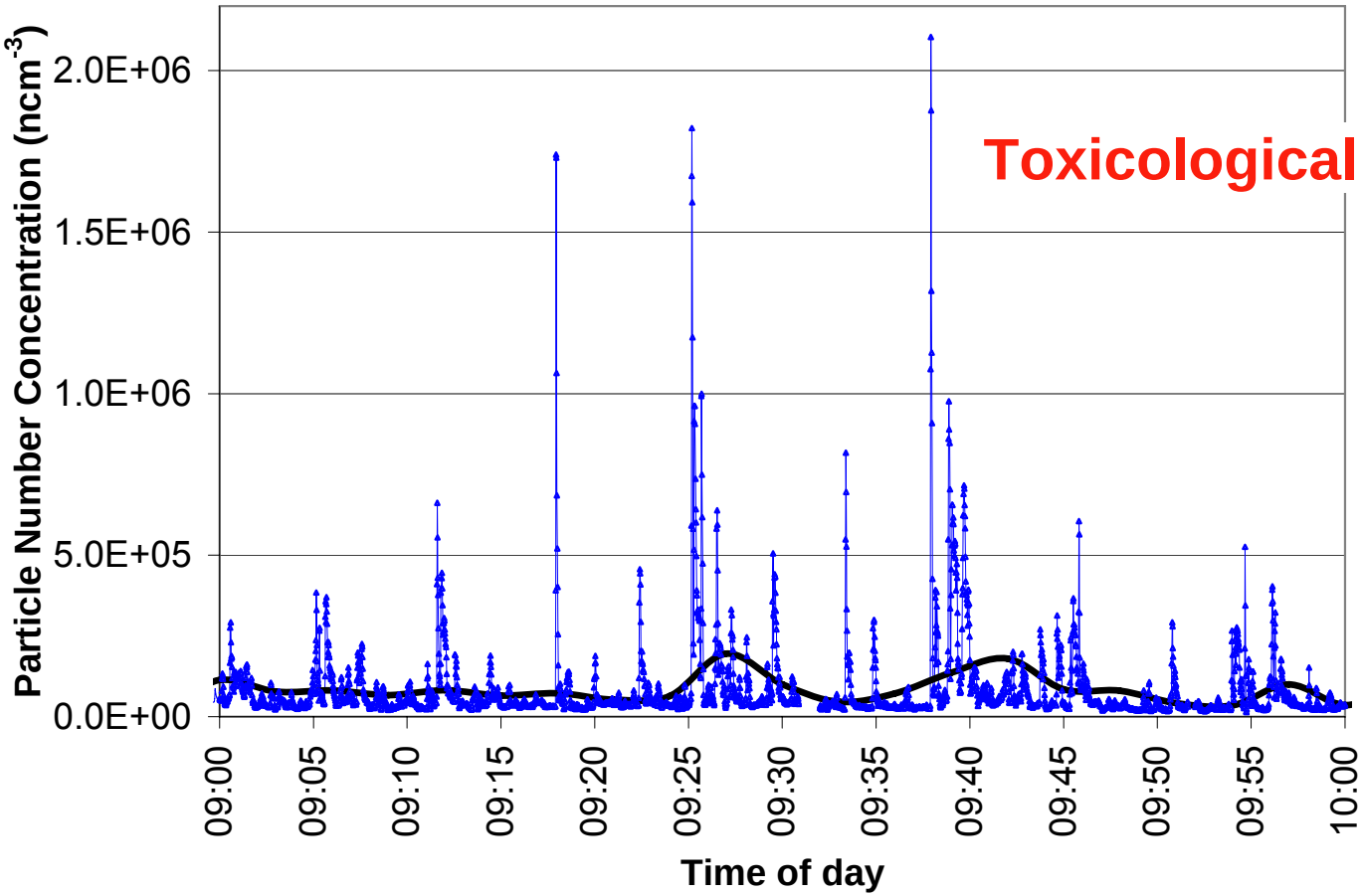
1 s and 3 min average PNCs on Narborough Road, Leicester, 2005.

SMPS - 3 min averages – not representative of short term peaks.

DMS (y) to CPC (x): y = 0.97x (R^2 = 0.82)

SMPS (y) to CPC (x): y = 0.62x (R^2 = 0.52), 24 hrly average.



Toxicological significance?????

Nature of roadside exposure to PNC – contribution of transient peaks to total concentrations

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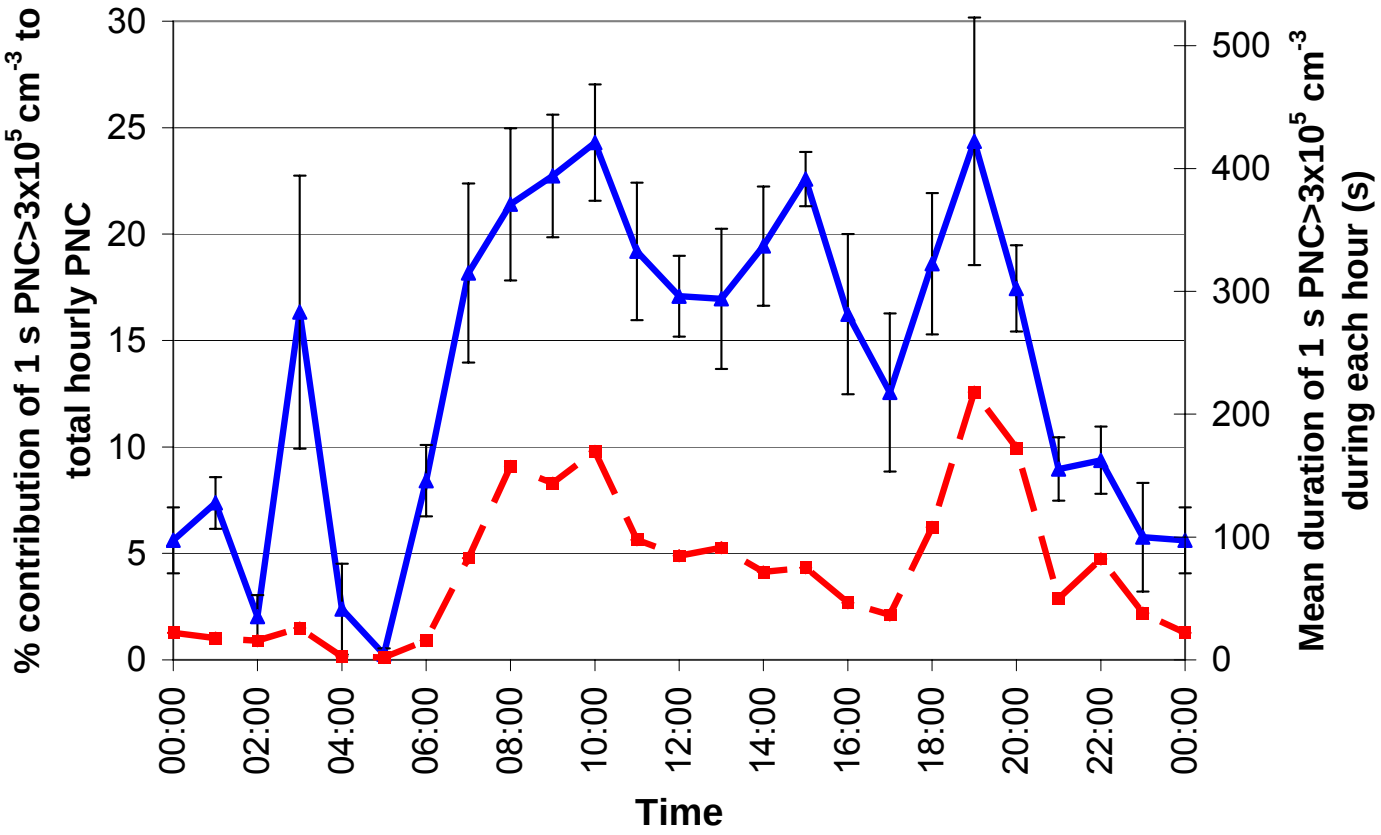

Average contribution of 1 s PNC > 3 x 10^5 cm^{-3} (blue) to hourly PNC.
Mean duration per hour of exceedences (red) over all data for NR.

Nature of transient peaks depends on source characteristics and dilution conditions

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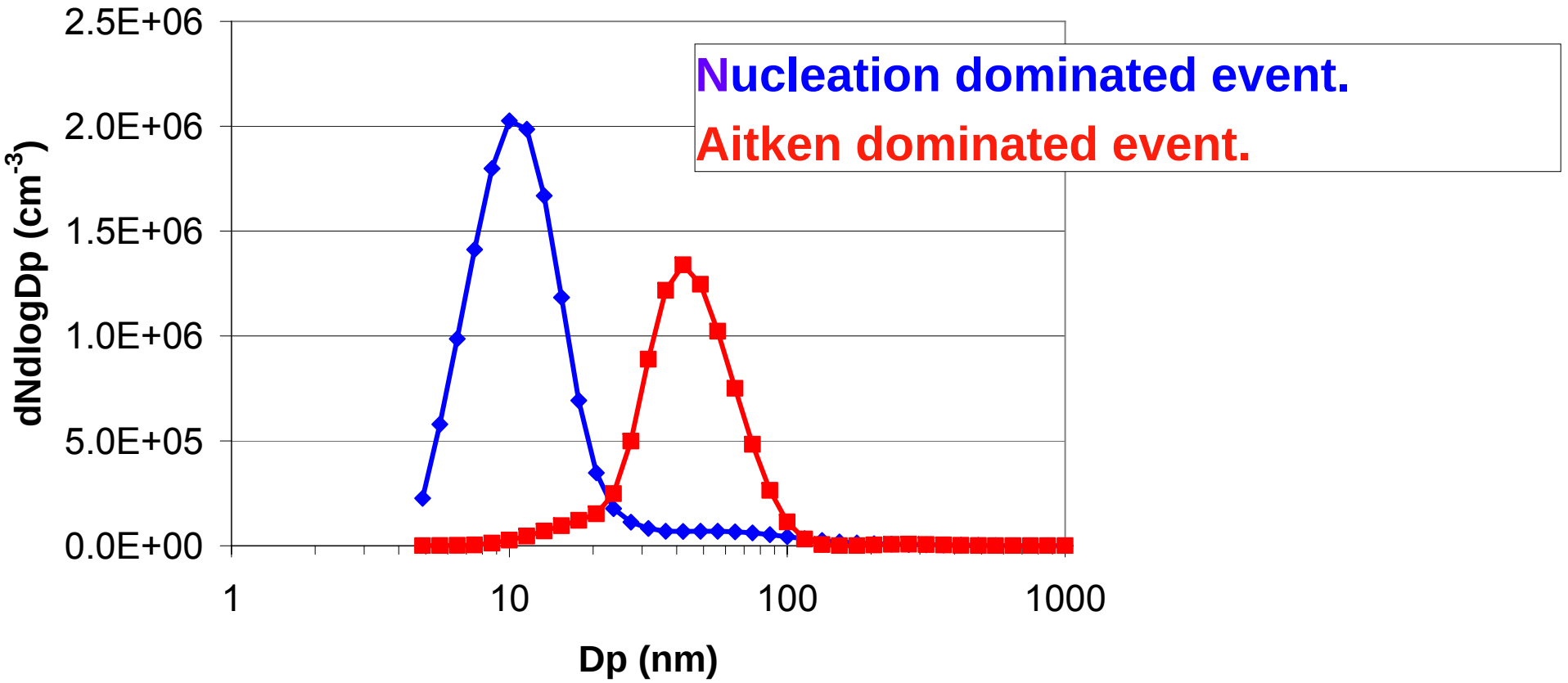

Particle size distributions (4th March 2005)
1 second means at peak of an elevated number concentration event.

Source related size distributions at urban roadside

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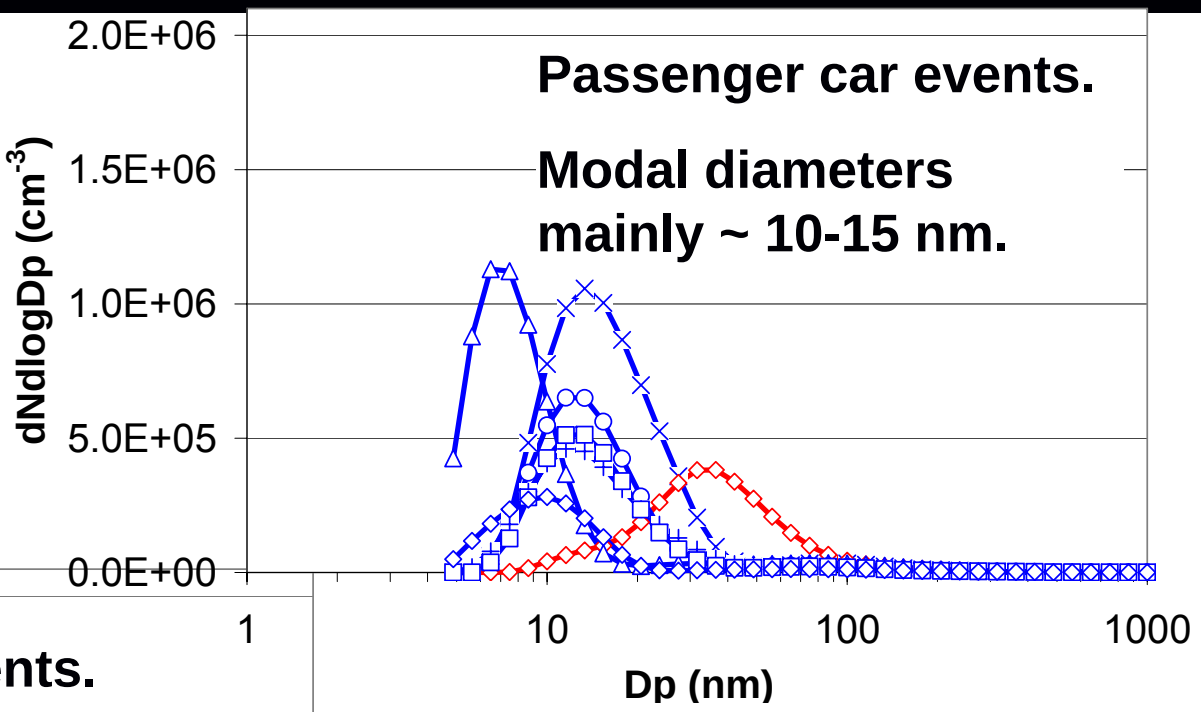
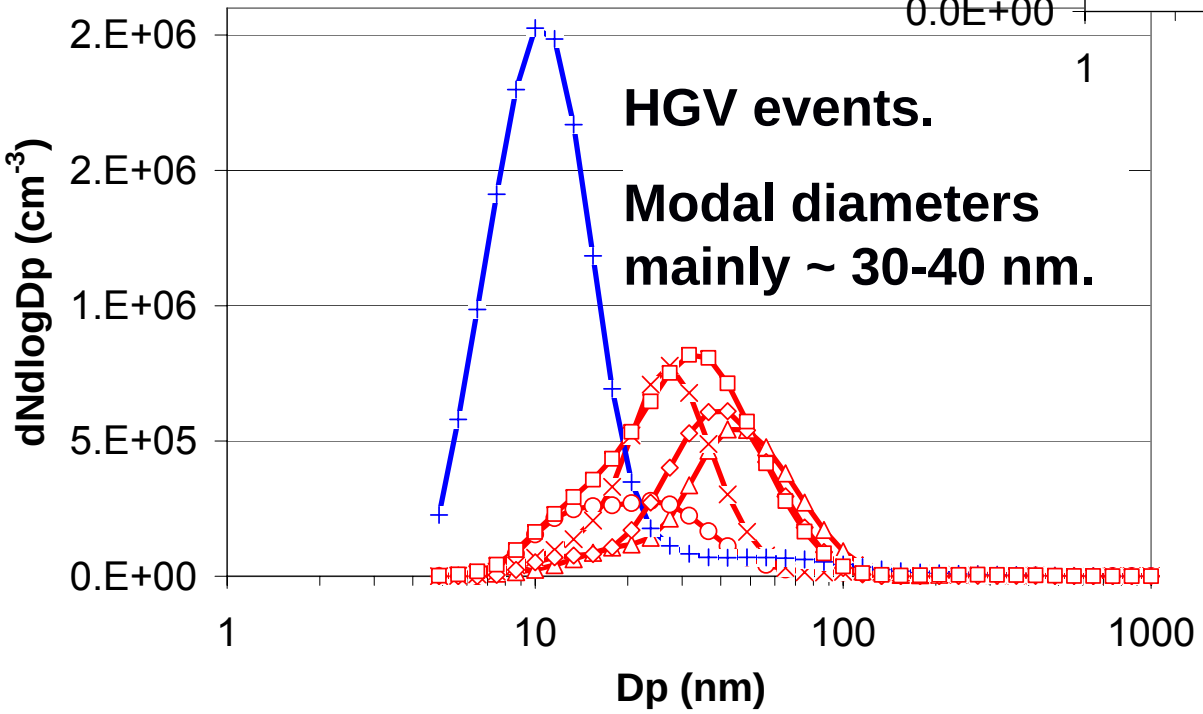
Will be differences in chemical nature of particles within different modes.

Toxicological Significance?





Contribution of modes to transient peaks at urban roadside (Leicester)

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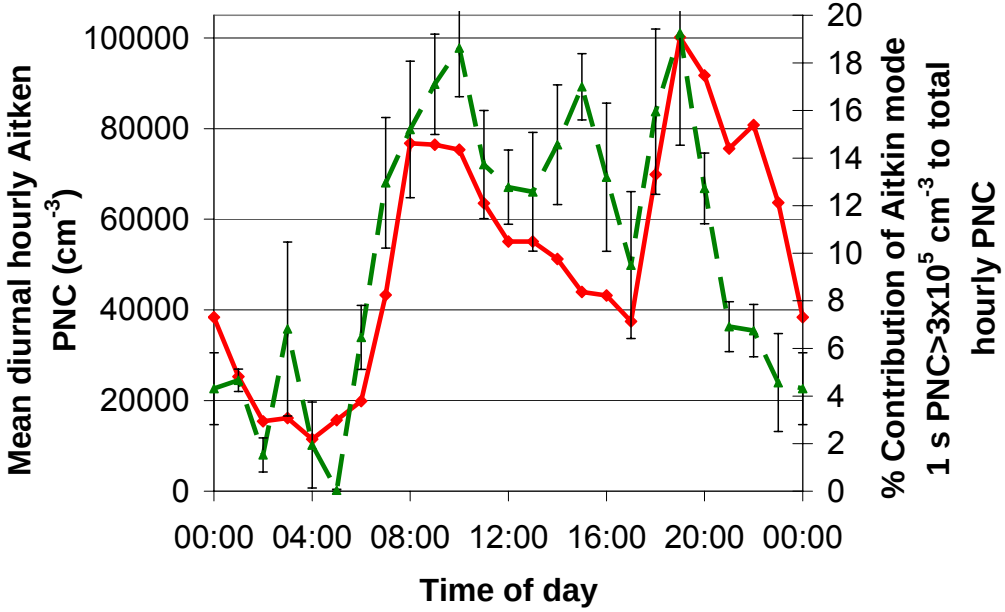
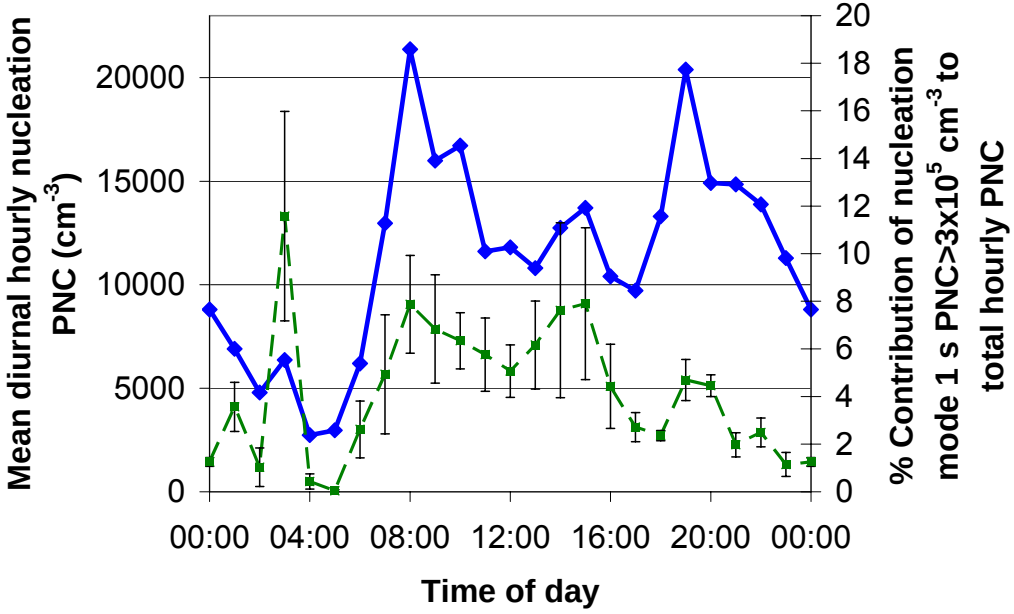
Up to 30% of hourly PNC is due to transient peaks > 3 x 10^5 cm^{-3}

In general Aitken mode events tend to dominate the transient peaks

Nucleation mode increases in importance overnight.





Relationship between hourly averaged traffic and PNC (Leicester)

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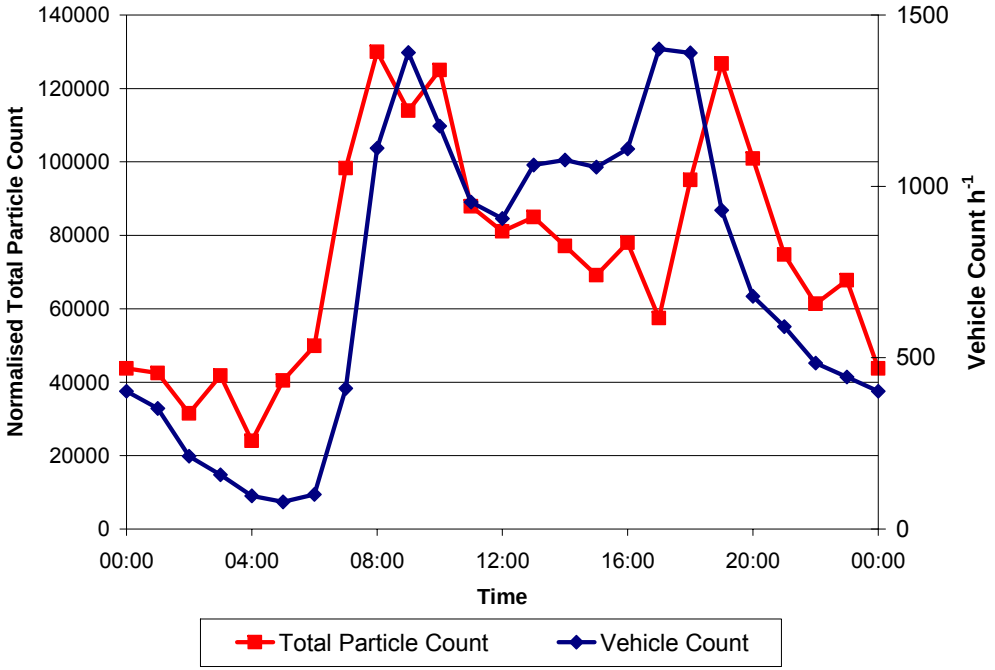
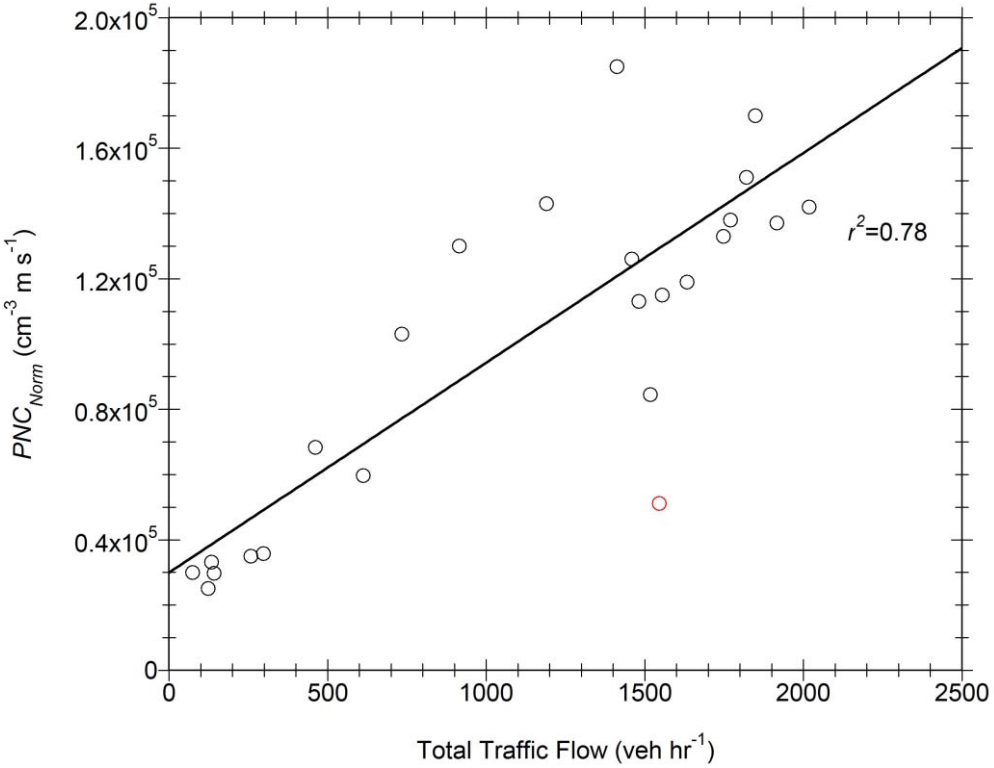
Here PNC has been normalised by wind speed which improves the relationship with traffic flows.





Influence of volatility characteristics

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The TEOM is affected by particle volatility since it heats the sample to 50°C.

Although corrections are made to account for volatile losses are these averaged corrections valid?

Suggested Euro VI emissions legislation indicates that denuded samples should be used to assess PNC tailpipe emissions.

- Reduces the influence of dilution on PNC.

If ambient measurements of PNC are taken should we use a denuder?

What would its influence be?

Daily ambient and denuded number concentration size distributions, Leeds Rd side

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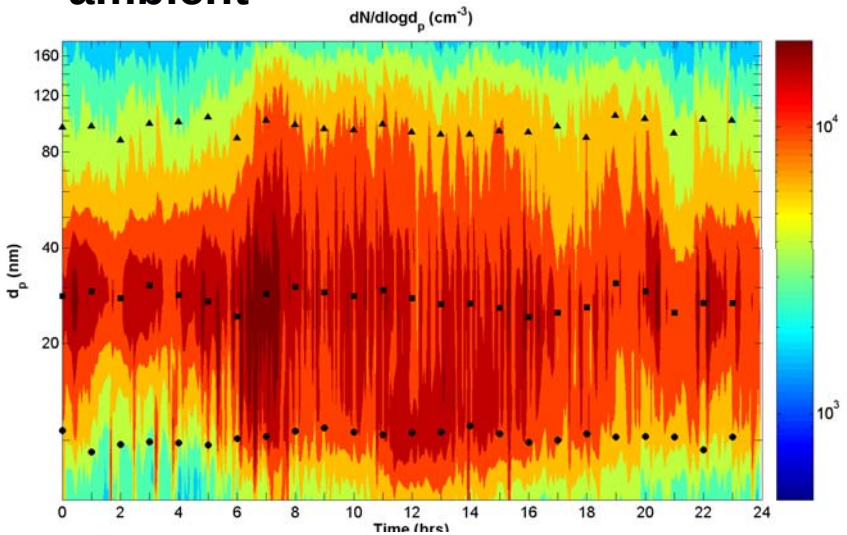
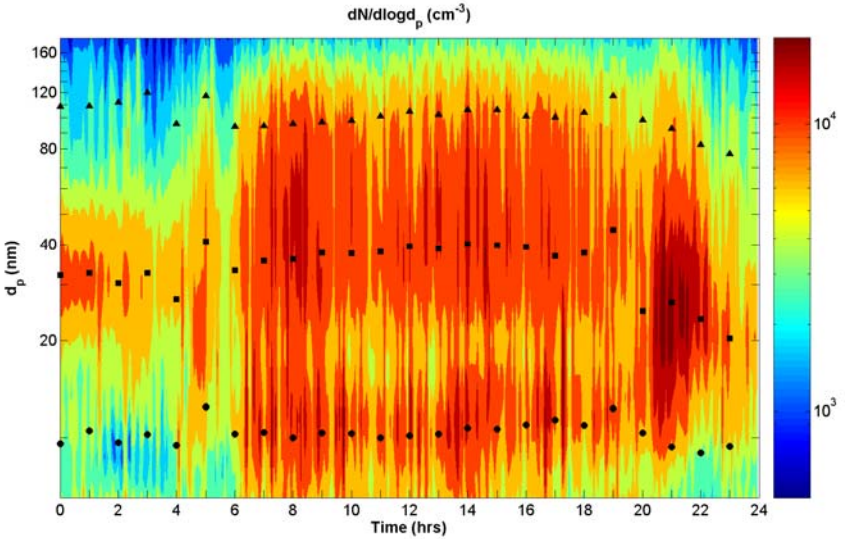
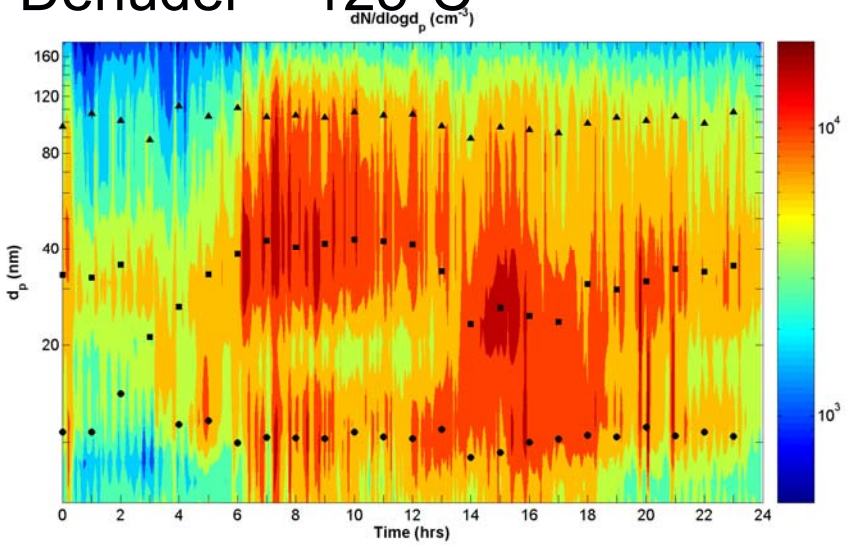
$T_{ambient}$



Denuder = 75°C



Denuder = 125°C



Strong daily variation in volatility.

- Photolytically driven nucleation mode in afternoon but is largely lost at 75°C
- Primary modes from morning rush hour still present at higher temps.
- Stronger separation of modes above 75°C, indicative of particle processing at ambient conditions.

Daily ambient and denuded number concentration size distributions, Leeds background

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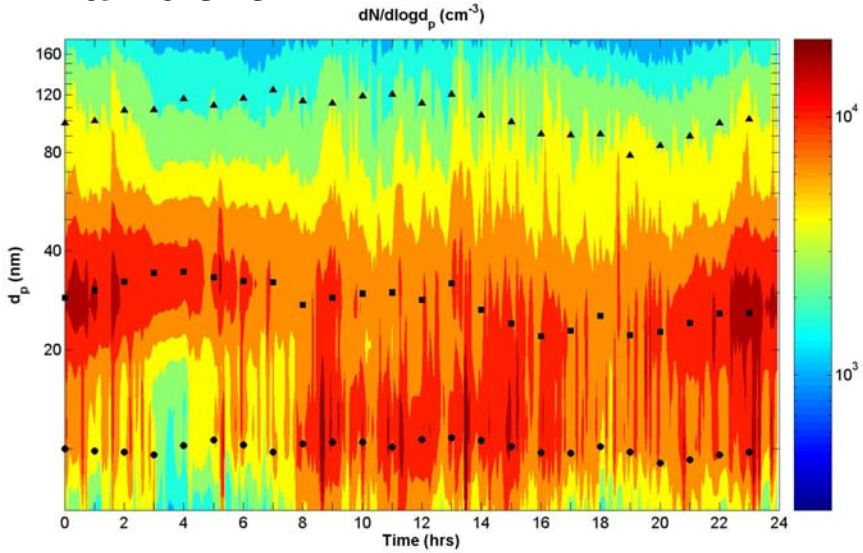
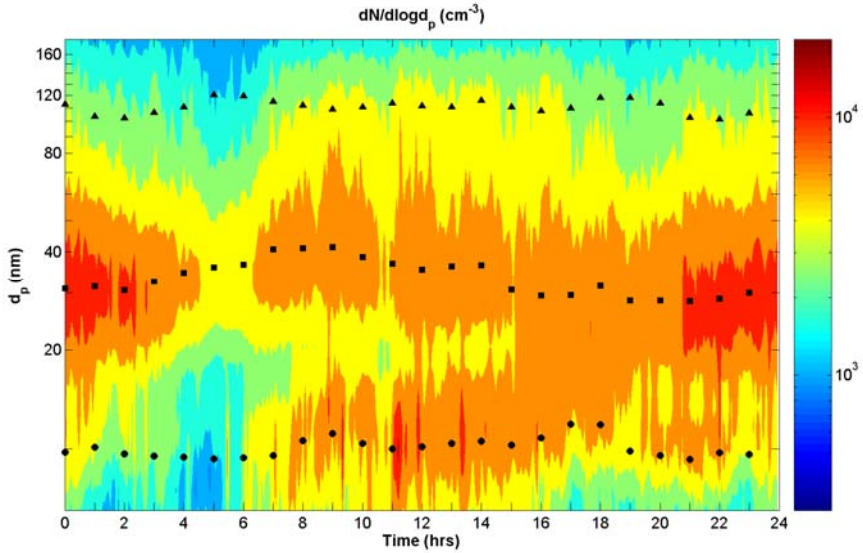
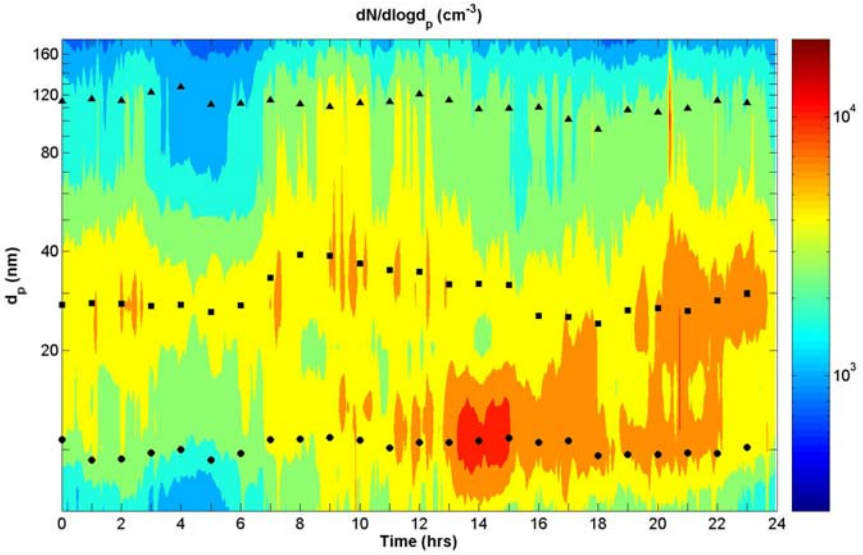
$T_{ambient}$



Denuder = 75°C



Denuder = 125°C



Still strong daily variation in volatility.

- Nucleation mode more prominent during daytime.
- Growth of particles is visible in denuded samples.
- More significant loss of particle numbers than at roadside.

Normalised reduction in PNC resulting from thermal treatment

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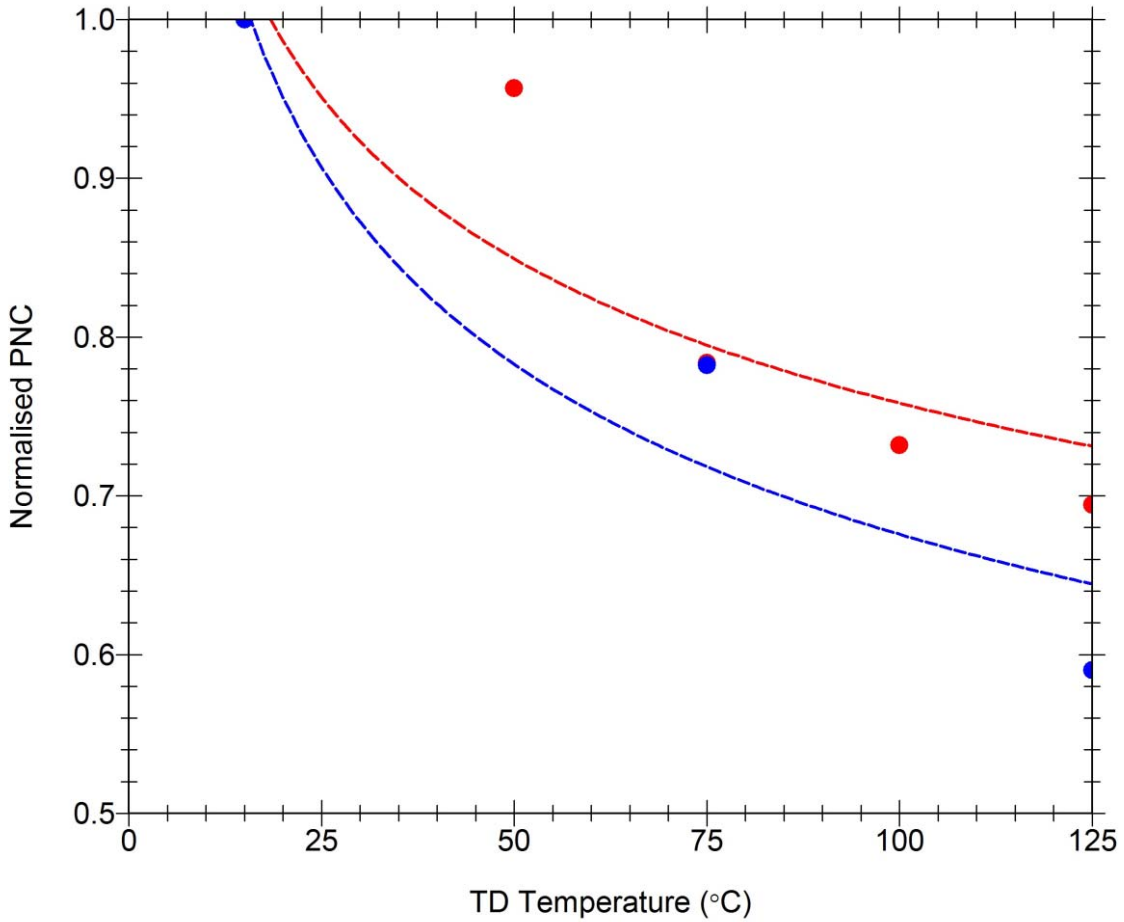

● Normalised roadside PNC; ● Normalised background PNC

- - - Exponential decay at roadside; - - - Exponential decay at background

Impacts of denuder

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- Heating the sample certainly removes the more volatile material potentially stripping the (less toxic ??) liquid droplets in the nucleation mode.
- Fairly high temperatures needed to strip the primary nucleation mode particles.
- Clearly differences in roadside and background chemical composition of semi-volatiles due to differing sources and atmospheric processing.
- Toxicological effects of condensed material on internally mixed particles should also be considered. **Is it understood?**
- Denuding to achieve consistent air quality number measurements would potentially be complex.
- Would it lead to PNC of essentially more toxic particles?
- How well do mass based measurements represent the numbers/surface area of the potentially more toxic Aitken mode particles?

Relationship between Aitken PNC and mass concentrations at roadside

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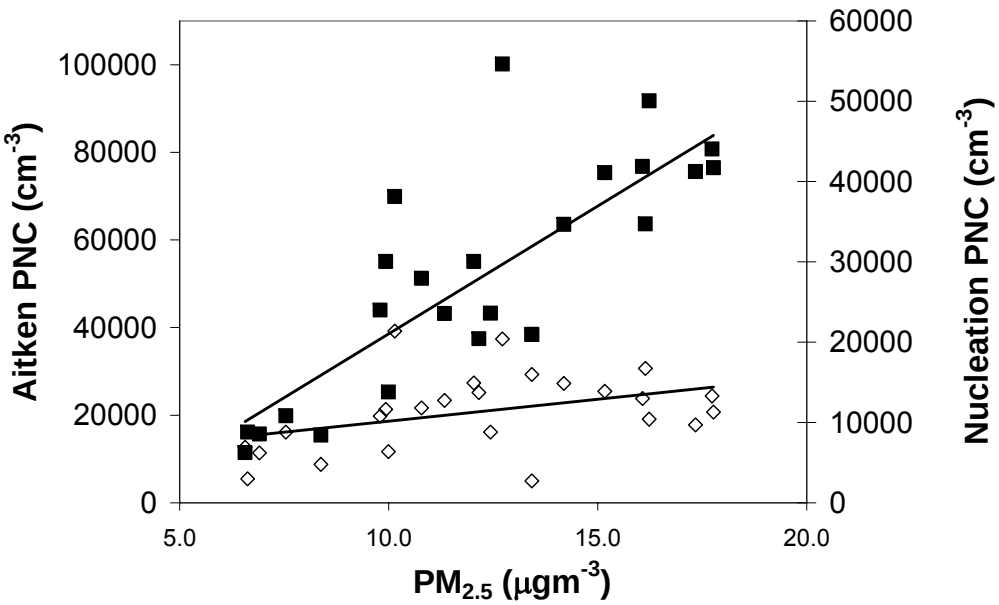

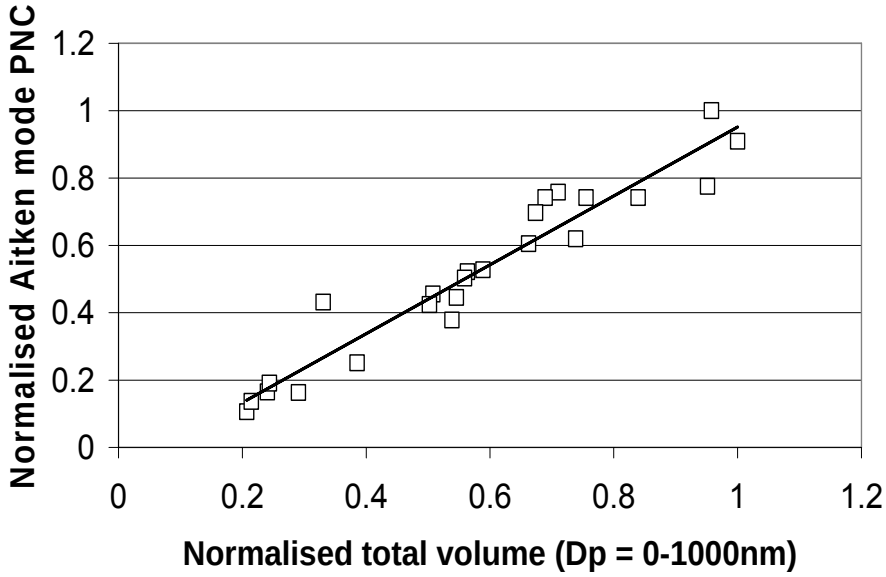

Weekday relationship between hourly diurnal average PNC and $PM_{2.5}$ on NR

■ – Aitken mode (R^2 = 0.65)

◊ – nucleation mode (R^2 = 0.16).

Relationship between normalised diurnally averaged hourly Aitken mode PNC and estimated normalised volume (up to 1µm) on NR (R^2 = 0.92).

Conclusions

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- **PNCs are strongly affected by dilution conditions**, pre-existing particle concentrations and the availability of semi-volatile material.
- Whilst semi-volatile material can be denuded, the influence of denuder temperature on PNC varies with time of day and source location.
- The transient nature of primary emissions and turbulent mixing leads to significant **short term excursions in PNC** that may affect the choice of measurement technique for both PNC and size distributions.
- A greater understanding of the **relative toxicity of particle modes** (Aitken, nucleation) etc. would contribute to the debate on appropriate metrics.
- Information on the influence of short term peaks would contribute to possible choice of instrumentation.
- If it is assumed that the internally mixed Aitken mode is more harmful then denuding would reduce the influence of the nucleation mode.
- On the other hand, mass based measurements correlate well with Aitken mode PNC compared to the nucleation mode.
- The contribution of nucleation mode and other semi-volatile material may be one reason for lack of consistency within epidemiological studies based on PNC.