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Introduction

1. Atmospheric particles influence climate; and cause adverse effects on human health, especially in urban areas.

2. Recently, particle size distribution and number concentrations in many cities in the world have been measured [e.g., 1,2, 3]. However, there is little information available about particles smaller than 10 nm.

3. The knowledge of ultrafine particles of < 10 nm in urban atmosphere is also important both to health concerns and atmosphere /aerosol science.

4. This paper introduce an investigation of sources and concentrations of ultrafine particles in urban air. The performance of particle measurement instruments is also discussed.

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[1] Morawska L, Thomas S, Bofinger N, Wainwright D and Neale D. Atmos. Environ. **1998**, 32, 2467-2478.
[2] Hughes L, Cass G R,Gone J, Ames M and Olmez **1998**, Environ. Sci. Technol. 32 1153-1161.
[3] Shi J P, Khan A A and Harrison R M. **1999**, Sci. Tot. Environ. In press.

Experimental

1. Instruments

- Ultrafine condensation particle counter (UCPC, TSI Model 3025, 50% cut-off size 3 nm).

- Condensation particle counter (CPC, TSI Model 3022A, 50% cut-off size 7 nm).

- Scanning Mobility Particle Sizer (SMPS, TSI Model 3071 Electrostatic Classifier, CPC 3022A, measuring range 9.5 - 358 nm))

- Epiphaniometer (measure Fuchs surface area).

- Sulphur dioxide (SO_2) analyser (Model-100, Enviro Technology)

- Nitrogen oxides (NOx) analyser (AC 30M, Environment s.a)

- A mini meteorological station (CR10, Campbell Scientific Ltd)

2. Monitoring sites

- Busy roadside, Site A (3m from kerb) and Site C (4m from kerb) (see Fig. 1)

- Near a busy road, Site B (25m from kerb) (see Fig. 1)

- Urban background, Site D (PUMA* campaign site, 10m height) (see Fig. 2)

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* PUMA---Pollution of the Urban Midlands Atmosphere

Results and Discussion

I. Concentration of ultrafine particles in urban air

1. Ultrafine particle number concentration and size distribution measured at a busy roadside (Site A, three metres from kerb).

a) The measurements are shown in Figure 3. Site A was in the upwind of the traffic at the sampling period.

b) The means and ratios, averaged over the whole sampling period, are shown below:

UCPC (>3 nm)	$1.7 \pm 0.6 \times 10^5$ cm^{-3}
CPC (> 7nm)	$9.5 \pm 3.5 \times 10^4$ cm^{-3}
SMPS (9.5-358 nm)	$4.7 \pm 2.4 \times 10^4$ cm^{-3}
(UCPC-CPC)/UCPC	0.44
SMPS / CPC	0.49
SMPS / UCPC	0.28

c) Results show that

- A large fraction (44%) of the measured particles were smaller than 10 nm*.

- SMPS only accounted for about half number of the particles measured by the CPC.

- Existing of particles smaller than 10 nm was also confirmed by the SMPS measurements (see Fig. 3 bottom graph).

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* Considering the loss of ultrafine particles in the sampling tubing and the CPCs measuring range, the real fraction should be higher than 44%.

2. Ultrafine particle number concentration measured at a site near a busy road (Site B, twenty-five metres from kerb, 50 metres from Site A)

a) The measurements are shown in Figure 4. From 9:36-12:00, the wind blew from Site A to Site B, and both Site A and Site B were in the downwind of the traffic.

b) The means and ratios, averaged over the period 10:00 – 12:00, are shown below:

	Site A	Site B
UCPC (>3 nm)	$> 2.4 \times 10^5$ cm^{-3}	$1.4 \pm 0.4 \times 10^5$ cm^{-3}
CPC (> 7nm)	$2.3 \pm 1.2 \times 10^5$ cm^{-3}	$8.9 \pm 2.9 \times 10^4$cm^{-3}
(UCPC-CPC)/UCPC		0.36

c) Figure 4 shows that

- About 36% of the measured particles were smaller than 10 nm at a site about 25 - 50 metres downwind the traffic.

- The Fuchs surface area increased simultaneously with the number concentration.

- NOx and SO_2 are good indications of traffic influence.

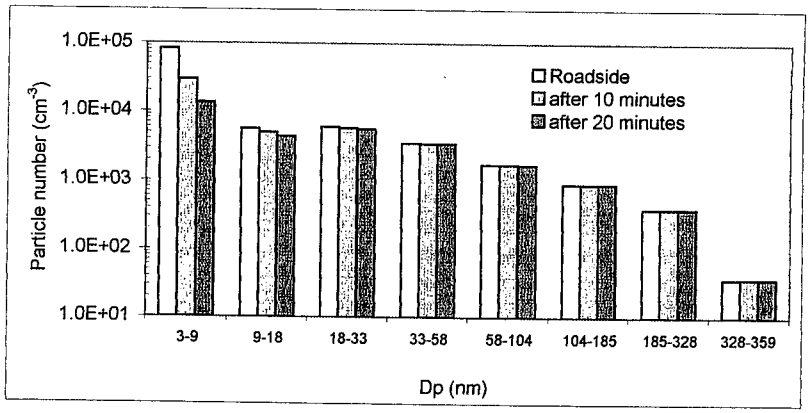
3. Ultrafine particle number concentration at urban background site (Site D, 10 metres height).

The measurements show that at most time, particle concentrations measured with CPC and UCPC were at a similar level. However, the sudden burst of the particle number concentration during lunch time in sunny days was observed. The burst of ultrafine particles of < 10 nm is probably due to homogeneous nucleation, although the further investigation is still being carried on currently.

About 30% of the measured particles were smaller than 10 nm at the peak time.

4. Lifetime of traffic emitted ultrafine particles of < 10 nm in urban air. The measurements taken at Site C (4m from Kerb) were used as modelling input.

a) Modelling results



b) Only Brownian coagulation was considered in the modelling (assuming no dilution). Initial particle size distribution was obtained from the SMPS, CPC and UCPC measurements averaged over the whole sampling period (10.5 hours). The model prediction shows that the lifetime (1/e) of particles smaller than 10 nm is about 10 minutes.

II. Sources of ultrafine particles in urban air

1. Road traffic

• Road traffic is a main source of ultrafine particles of smaller than 10 nm.

• Evidence shows that both diesel and petrol vehicles emit ultrafine Particles of < 10 nm [(1)].

2. Combustion point sources

• There are two elevated point sources within the campus, one of them, shown in Figure 1, is burning nature gas and heavy oil. The distance between the chimney and Site A is about 200 metres.

• It is found that ultrafine particles of < 10 nm were associated with wind direction of about 290 degree and SO_2 (not NOx), as shown in Figure 5. This indicates that the chimney emission is the source of ultrafine particles of < 10 nm.

3. Homogeneous nucleation ?

• There is little direct evidence of new particle formation through homogeneous nucleation in urban air due to relatively high concentration of pre-existing particles in urban air.

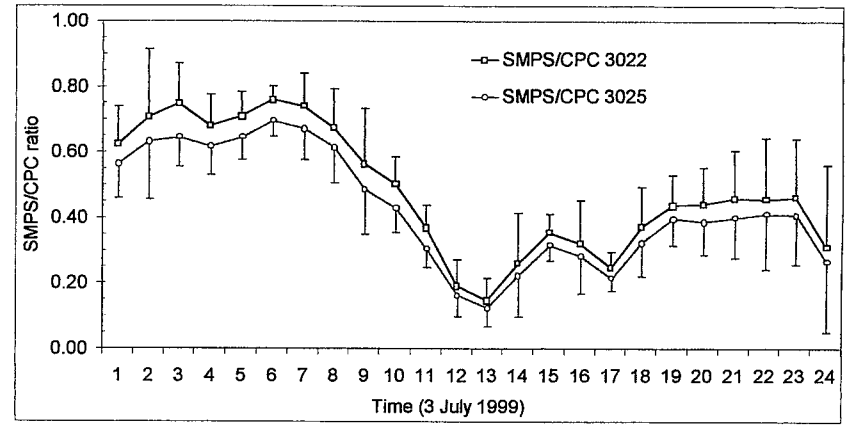
• Particle number concentration bursts were measured at Site D. Preliminary analysis shows that homogeneous nucleation probably accounts for the formation of ultrafine particles of < 10 nm.

(1) Shi J P and Harrison R M, (1999) Unpublished data.

III. Performance of SMPS, CPC and UCPC in particle number measurements

Ratio of SMPS to CPC and UCPC

• The Ratios of SMPS/CPC and SMPS/UCPC are not constants, they are various with time, as shown below (measured at Site D):



• At Site D (urban background), hourly ratios averaged over 8 days are shown below:

$$\text{SMPS/CPC} = 0.49 \pm 0.15$$
$$\text{SMPS/UCPC} = 0.43 \pm 0.14$$

• Generally, the ratios are lower when measurements were taken near the sources (primary and secondary). Considering the measuring range of SMPS (9.6-358 nm), CPC (>7 nm) and UCPC (> 3nm), this variation reveals the existing of ultrafine particles < 10 nm.

Conclusion

1. A high number density of ultrafine particles of < 10 nm can be measured in urban air, especially near their sources.

2. Vehicle emissions and combustion point sources are the main primary sources, and homogeneous nucleation may be a secondary source.

3. The composition of particles of < 10 nm is currently not known.

4. Evidences[1] show that ultrafine particles of < 10 nm can be formed during the dilution process of engine exhaust. Further study of the formation of ultrafine particles of < 10 nm (both primary and secondary) in urban air is recommended.

Acknowledgement
This research was supported financially by Perkins Engines Company limited.

[1] Shi J P and Harrison R M (1999) Investigation of Ultrafine Particle Formation during Diesel Exhaust Dilution. Environ. Sci. Technol., in press.

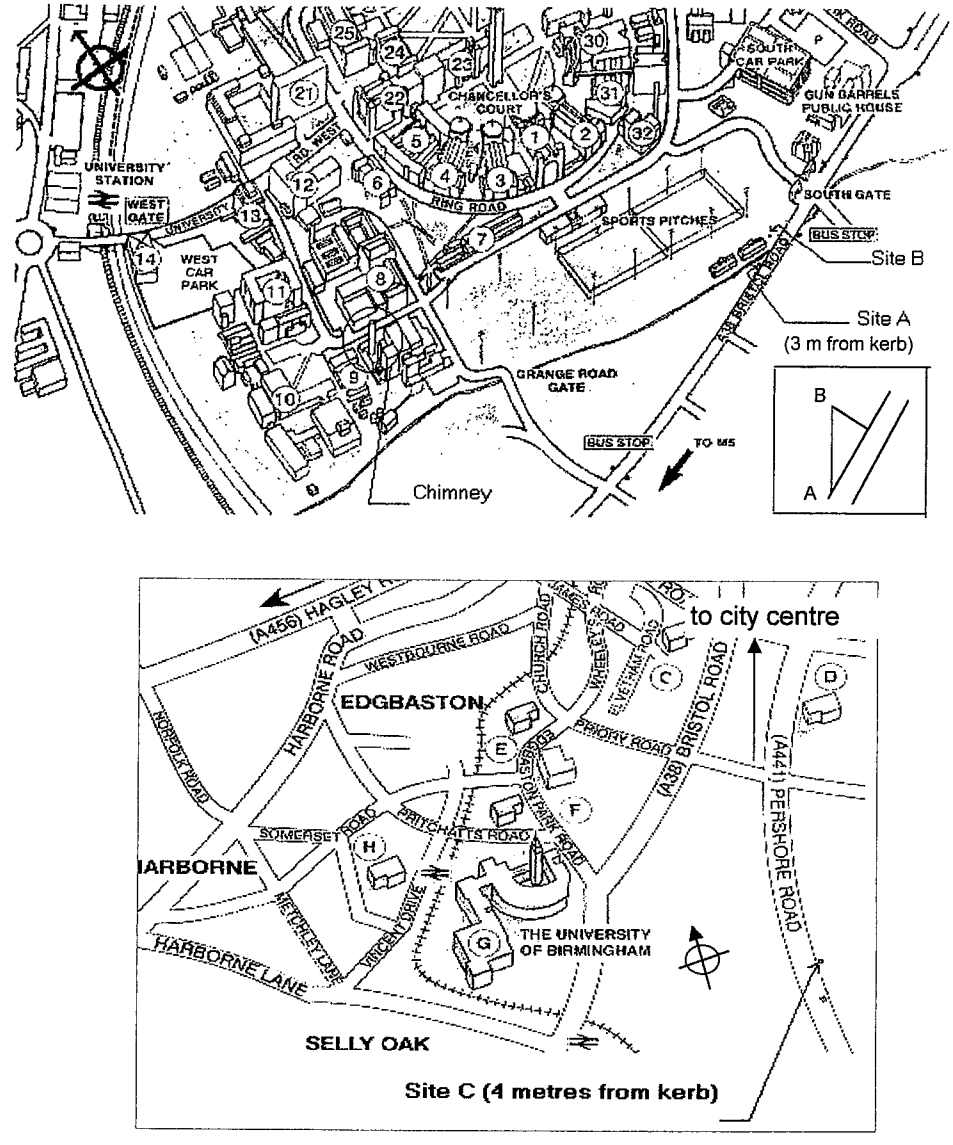
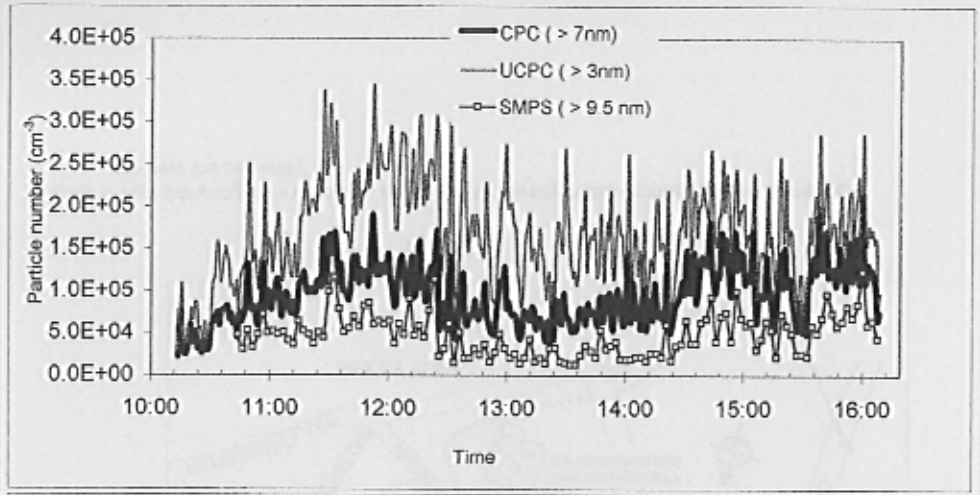
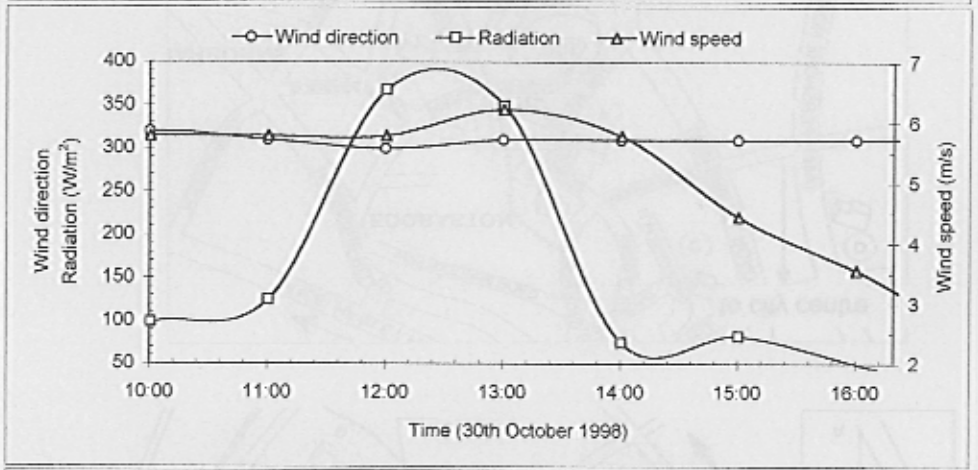


Figure 1. Top: Sampling sites inside the campus of University of Birmingham. Bottom: Sampling site near the university.

Figure 2. Urban background site, Site D.





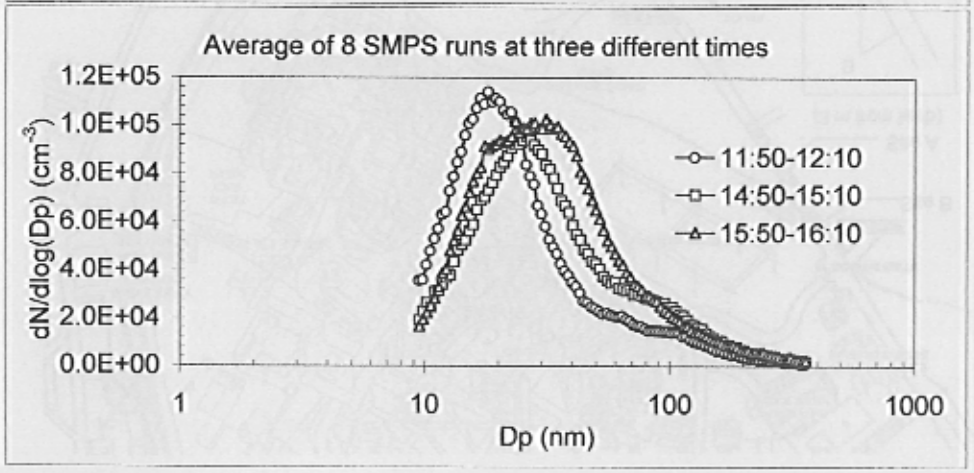


Figure 3. Particle concentration and size distribution measured at a busy road side (3m from kerb), associated with some met. data measured at 3 m height nearby.

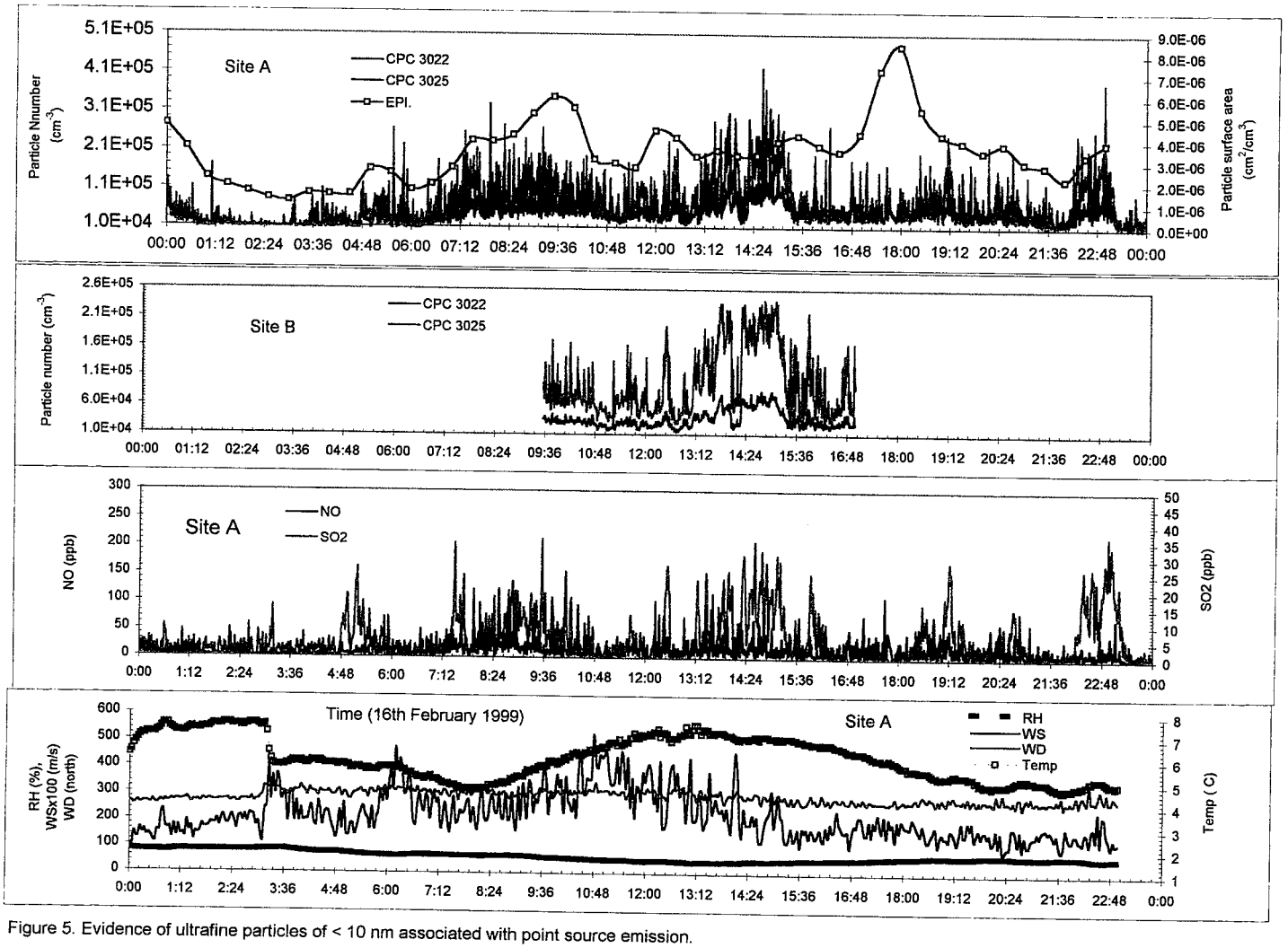


Figure 5. Evidence of ultrafine particles of < 10 nm associated with point source emission.

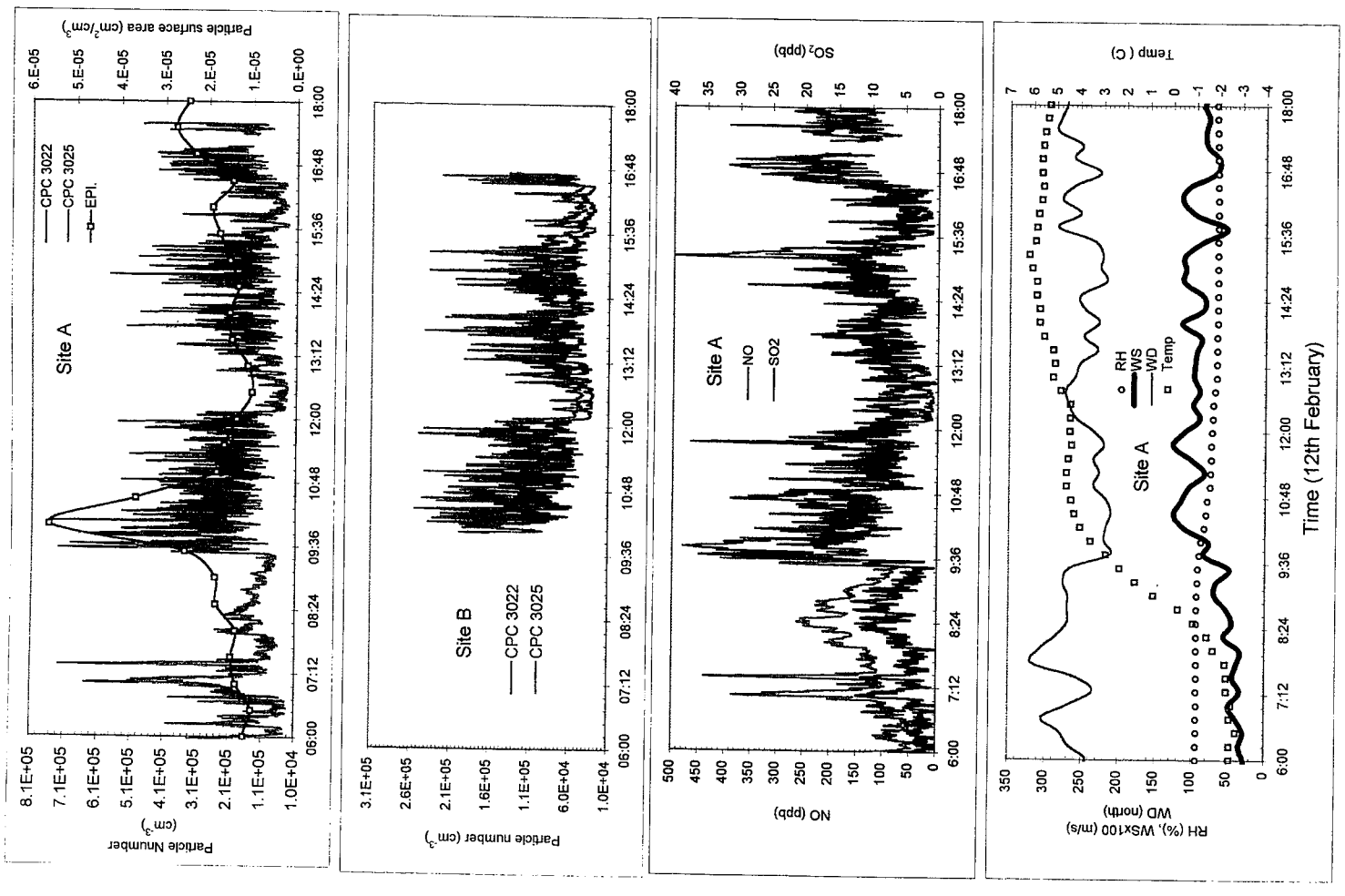


Figure 4. Measurements taken at Site A and Site B.