

## Measurements using broadband cavity-enhanced absorption spectroscopy of the sum of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> during REPARTEE II and associated model studies

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Keywords: Cavity enhanced absorption spectroscopy, Boundary Layer, Trace Gases, Urban Areas.

Cavity-enhanced absorption spectroscopy enables the unambiguous determination of gas concentrations at trace levels in both laboratory and field atmospheric studies. The versatility of this method has here been applied to the measurement of the nitrate radical (NO<sub>3</sub>) absorption band centred at 662nm, corresponding to its B<sup>2</sup>E'-X<sup>2</sup>A<sub>2</sub> electronic transition using broadband cavity-enhanced absorption spectroscopy (BBCEAS) (Ball *et al* 2004; Langridge *et al*, 2006). A heated inlet was used to shift the equilibrium between NO<sub>3</sub> and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) to convert all ambient N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub> to allow the sum of these species to be measured. The nitrate radical is rapidly photolysed during the day and generally only builds to appreciable concentrations at night, except for under extremely high O<sub>3</sub> concentrations. NO<sub>3</sub> is the predominant night-time oxidiser of volatile organic compounds and other species. Conversion of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> is also an important NO<sub>y</sub> removal mechanism as can be seen in figure 1.

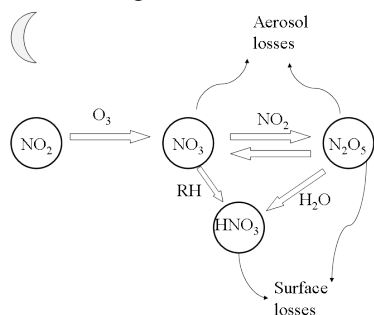


Figure 1 – A simplified schematic of night-time nitrate chemistry and the equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>.

Measurements were made in an urban area at an altitude of 189m on balcony of the 35th Floor of the British Telecommunications (BT) Tower, London, during October and November 2007 as part of the second phase of the Regent's Park and Tower Campaign (REPARTEE II). A BBCEAS instrument, using a ~665nm LED light-source was deployed during this campaign. Calibration of the mirror reflectivity as a function of wavelength was required on a daily basis to account for build up of particulates on the high finesse mirrors although they were purged with nitrogen to reduce this effect. Mirror

reflectivity,  $R(\lambda)$ , was derived from the phase-shift between the cavity output and the modulated LED source. Beer-Lambert retrieval over a range of wavelengths was used to retrieve absorber concentrations in every 10s sample from an absorption spectrum as shown in figure 2.

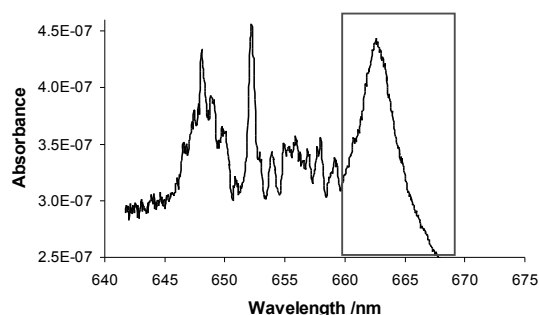


Figure 2 – An example absorbance spectrum from REPARTEE II depicting 4n+d polyad bands of H<sub>2</sub>O and the NO<sub>3</sub> absorption band (boxed).

Ancillary measurements of nitrogen dioxide, pressure and temperature were used to infer the NO<sub>3</sub>:N<sub>2</sub>O<sub>5</sub> ratio. Wall losses have been determined for similar laboratory experiments to be ~20%. The data collated shows large variation in night-time concentrations of the sum of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, (the vast majority of this being N<sub>2</sub>O<sub>5</sub>), with some very high concentrations measured, often peaking at 1-2ppb with one night (30-31/10/2007) at ~8ppb. These measurements have important implications for the oxidative processes of the night-time boundary layer. Large-scale chemical models such as pTOMCAT currently reproduce the diurnal variability of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> concentrations but predict very small concentrations (~2ppt maximum). Box-model studies were used to investigate the chemical scenarios developing such high N<sub>2</sub>O<sub>5</sub> concentrations.

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Ball, S. M., Langridge, J. M., & Jones, R.L. (2004). *Chem. Phys. Lett.*, 398, 68–74.

Langridge, J. M., Ball, S. M., & Jones, R.L. (2006). *Analyst*, 131, 8, 916-922.

## Chemically-speciated aerosol fluxes above three UK cities

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Keywords: aerosol mass spectrometry, eddy covariance fluxes, organic aerosol, urban aerosol, traffic emission.

There is considerable uncertainty regarding the processes controlling the formation and transformation of organic aerosol (OA) in the atmosphere. Regional aerosol, advected into the city, mixes with the primary urban emissions of particles and VOCs to create an environment where particle composition is controlled by a number of factors, not least chemistry and complex urban meteorology. Measurements of chemically-speciated particle fluxes above urban areas can give us insight into exchanges between urban centres and the free troposphere, as well as the chemical and physical processing which occurs during transport.

We present chemically-speciated aerosol fluxes and concentrations measured three contrasting cities in the United Kingdom. An aerodyne quadrupole-AMS was deployed on a tall building in the three urban centers; the Nelson Monument in Edinburgh, the Portland Tower in Manchester and the BT Tower in London. We use the coupled eddy covariance-AMS system as described in Nemitz *et al.*, 2008 to measure the flux of non-refractory (NR) PM<sub>1</sub> above the three cities. Supporting measurements of CO and CO<sub>2</sub> fluxes made by eddy covariance are also presented and emission factors relative to these pollution tracers have been calculated.

The organic aerosol component of the NR-PM<sub>1</sub> mass has been further analysed using statistical techniques to ascertain the contribution to the OA flux and concentration of so-called hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA). OA dominates the mass of PM<sub>1</sub> in all three cities with nitrate the next major component of the mass in Edinburgh and Manchester and sulfate the next major component in London. HOA dominates the OA mass in Edinburgh and for some time periods in Manchester, in contrast to the finding of Zhang *et al.*, for urban areas and situation in London where OOA was the larger proportion of the OA mass.

At all locations, HOA has a large relative emission flux relative to OOA. The HOA fluxes are generally upward and show diurnal trend. Average flux densities of hydrocarbon-like organic aerosol (HOA) range from 63 ng m<sup>-2</sup> s<sup>-1</sup> in Edinburgh to 440 ng m<sup>-2</sup> s<sup>-1</sup> in London. Excellent

correlation was found between emission fluxes of CO and CO<sub>2</sub>. However, HOA fluxes show a much weaker correlation with these gases. Changes in the relative emission strengths of HOA and CO<sub>2</sub> are likely related to changes in the fuel mix, vehicle fleet and the changing contribution of building heating. However, the relatively constant CO/CO<sub>2</sub> flux ratio suggests that i) these changes were not pronounced and ii) was without a significant biogenic component; implying the CO<sub>2</sub> emission flux was due mainly to combustion. Assuming that both HOA and CO<sub>2</sub> (and CO) originate from similar sources, the measurements suggest that HOA undergoes considerable processing between emission and measurement of the flux high above the urban centre. The fraction of HOA that is evaporated and/or chemically processed is likely to depend on measurement height, temperature, radiation, photochemistry, and transport time-scale. Nevertheless, as the transport time-scale during these measurements is on the order of minutes to tens of minutes, the flux ratio HOA/CO<sub>2</sub> is likely to be more representative than emission ratios derived from urban concentration ratios, which accumulate over tens of minutes to hours. Emission ratios range from 0.24 to 1.37 g (kg C)<sup>-1</sup>.

The authors thank BT, Edinburgh City Council and Bruntwood for logistical support and access to the field sites. This work was funded by the NERC CityFlux project and the BT tower deployment was also part of the REPARTEE experiment described by Harrison *et al.* in this session.

Nemitz, E.; Jimenez, J.L.; Huffman, J.A.; Canagaratna, M.R.; Worsnop, D.R.; Guenther, A.B. (2008). *Aerosol Science and Technology*, **42** (8), 636-657.

Zhang *et al.*, (2007). *Geophysical Research Letters*, **34**, L13801, doi:10.1029/2007GL029979

## Attribution of Organic Aerosols in UK Cities

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Keywords: Aerosol Characterisation, Aerosol Mass Spectrometry, Organic Aerosols, PMF, Urban Aerosols

Organic matter represents a major fraction of particulates in urban environments, however attempts to quantitatively predict their loadings remains elusive (Volkamer *et al.*, 2006). Part of the problem is that we still lack effective ways of comprehensively and unambiguously characterising the fraction in terms of the compounds present, the functionality and the sources. Recently the technique of positive matrix factorisation (PMF) has been employed for source apportionment of aerosols and this has been shown to be highly useful when used with organic data from the Aerodyne Aerosol Mass Spectrometer (AMS) (Lanz *et al.*, 2007).

Traditionally, organic AMS data in polluted environments has been split into hydrocarbon-like and oxygenated organic aerosols (HOA and OOA) which in turn has been ascribed to primary and secondary organic aerosols respectively (Zhang *et al.*, 2005). The use of PMF, which can deliver many factors, has shown that many more fractions can be identified and quantified. The technique has also benefited from the use of time-of-flight mass spectrometers through the increase in signal-to-noise they provide (Drewnick *et al.*, 2005).

It is known that the importance of various sources and processes vary according to geographical location and meteorology. It is therefore important to characterise the organic aerosols as extensively as possible, using data from multiple measurement campaigns. To this end, this paper presents the analysis from a number of recent studies using time-of-flight AMS instruments, including the REPARTEE experiments in London and CityFlux in Manchester during 2006 and 2007. These data were collected in conjunction with measurements of aerosol number, size distribution, equivalent black carbon mass and single particle composition (using an ATOFMS). Locations used included roadside measurements on a busy bus corridor, roof level in the city centre and urban parkland.

Several differences and similarities were noted between the different datasets. Notably, in addition to the usual HOA, OOA1 and OOA2 factors normally associated with combustion and secondary organic aerosols, an additional factor was isolated that could be associated with cooking, based on diurnal profile and similarity of its mass spectra to previously reported cooking spectra. The fractional contribution of this during the REPARTEE 1 study

was comparable to that of the primary organics from the transport sector (figure 1).

The primary factors could also be compared with measurements of carbon monoxide and black carbon to derive emission ratios representative of the sources (using roadside measurements) and the grid-scale cohort emissions (using roof-level measurements).

In common with most urban studies, large contributions from secondary organics were noted. In addition, potential biomass burning signatures were seen in Manchester, possibly coming from sources outside of the city.

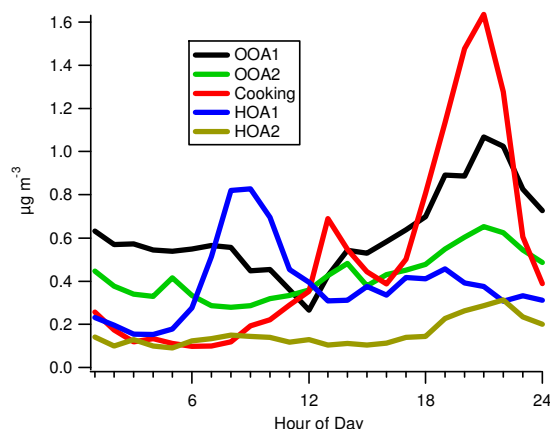


Figure 1: Median diurnal profiles from a 5-factor analysis of the REPARTEE 1 dataset in London.

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Drewnick, F., *et al.* (2005), *Aerosol Sci. Technol.*, 39, 637-658.

Lanz, V. A., *et al.* (2007), *Atmos. Chem. Phys.*, 7(6), 1503-1522.

Volkamer, R., *et al.* (2006), *Geophys. Res. Lett.*, 33(17), 4.

Zhang, Q., *et al.* (2005), *Environ. Sci. Technol.*, 39(13), 4938-4952.

## Real time chemical characterisation of aerosols via ATOFMS and ToF-AMS during REPARTEE I

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Keywords: Aerosol Mass Spectrometry, On Line Measurements, AMS, Aerosol Chemistry, Mixing State

The advent of techniques of particle mass spectrometry offers great insights into the source apportionment and atmospheric chemistry of aerosols. The aerosol time-of-flight mass spectrometer (ATOFMS) offered by TSI provides information on a polydisperse aerosol, acquiring precise aerodynamic diameter ( $\pm 1\%$ ) within the range 0.3 to 3 micrometres and individual particle positive and negative mass spectral data in real time. The AMS (Aerodyne Research, Inc.) provides online, real time measurements of the mass of non-refractory components of aerosol particles as function of their size. ATOFMS is capable of single particle analysis, whilst AMS requires the collection of an ensemble of particles to obtain sufficient sample for analysis. However, the AMS can quantify the size resolved organic carbon, sulphate, ammonium and nitrate mass loadings of aerosol in the size range between 60 and 600 nm. The data shown herein were collected at Regents Park (London-October 2006) during the REPARTEE I project. The general overview of the findings of the two particle mass spectrometers will be presented elsewhere. Herein, three main key findings will be presented.

1. The ATOFMS classified two types of nitrate-containing particles; one being formed locally, the other regionally transported from continental Europe. Local nitrate was formed at nighttime. AMS nitrate mass loading and ATOFMS total nitrate containing particles showed a very good correlation. The ATOFMS showed that the LRT nitrate particle type exhibits a diurnal temporal variation, evaporating during the day due to the higher temperature. However, the core of the LRT nitrate containing particles is still detected during the day and is composed mainly of elemental carbon and sulphate with a size distributions shifted towards smaller particles.

2. A fog event was monitored with state-of-the-art real-time aerosol mass spectrometers in an urban background location in London (England) during the REPARTEE-I experiment. Specific particle types rich in hydroxymethanesulphonate (HMS) were found only during the fog event. Formation of inorganic and organic secondary aerosol was observed as soon as fog was detected and

two different mechanisms are suggested to be responsible for the production of two different types of aerosol. Nitrate aerosol is produced in the liquid phase within fog droplets. Contrary to previous studies, the formation of HULIS was observed on interstitial particles but not in evaporated fog droplets, suggesting heterogeneous formation mechanisms depending on parameters other than the water content and not fully understood. Not only are secondary aerosol constituents produced during the fog event, but the primary aerosol is observed to be processed by the fog event, dramatically changing its chemical properties.

3. The application of the ART-2a neural network algorithm to the ATOFMS data characterized a specific particle type (rich in secondary organic aerosol and polycyclic aromatic compounds; SOA-PAH). The temporal trend of this particle type presented a strong weekday-weekend variation, suggesting a strong link with traffic emissions. Comparisons with several other measurements taken during the REPARTEE-I (including positive matrix factorization (PMF) analysis of the AMS data) excluded local primary anthropogenic sources. ATOFMS single particle mass spectra revealed a strong component of oxidized organic carbon, associated with PAH signals and flavonoids. This particle type was internally mixed with strong acidic sulphate species, but not with nitrate. Moreover, this particle type was found peaking only during the warmest part of the day (11.00-14.00) and is therefore thought to be influenced by photochemical reactions in the particle phase. The SOA-PAH particle type, rich in flavonoids, could suggest a mechanism for production of secondary organic aerosol from gas-phase reactions of PAH.

### ACKNOWLEDGEMENTS

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## The effect of boundary layer dynamics on the aerosol size distributions over London

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Keywords: Lidar, SMPS, Aerosol Size Distributions, Urban Aerosols, Boundary Layer

Urban air pollution is one of the environmental problems of major concern and will, due to growing urbanization, probably become more and more important in the future. So much that air pollution is a typically urban problem, so little is known concerning the flow and dispersion characteristics over urban surfaces. Lidar permits the detection of the BL top with a vertical resolution of a few meters and a temporal resolution in the range of seconds to minutes.

The lidar instrument used on the REPARTEE II campaign was a Halo Photonics 1.5 micron scanning Doppler lidar (provided by UFAM and operated by the University of Salford). It was installed in the car park of the University of Westminster building on the Marylebone Road and was running continuously for three weeks between the 24th of October and the 14th November 2007. Due to the proximity and height of the neighbouring buildings, the lidar was restricted to making only vertical stare measurements i.e. directly upwards. During this study the lidar had a vertical resolution of 30 metres, with 66 gates measuring up to 2 km into the atmosphere. The lidar returns a measurement every about 4 s consisting of 20,000 'integrations', or accumulated signals and it was restricted to vertically pointing measurements. However, different measurements were possible, including aerosol layer top, boundary layer top, convective mixing layer height, turbulent mixing layer height

Moreover, during the REPARTEE-II, 3 SMPS systems were used simultaneously at the road, park and tower sites. The SMPS systems were deployed concurrently at the three locations measuring particles with diameters over the size range 15.1 to 661 nm. The same SMPS models were used in Regents Park and on the BT tower (namely, DMA TSI 3080 and CPC TSI 3022A), which were different to that used at the Marylebone Road (namely, DMA TSI 3080 and CPC TSI 3776). The 3 different systems were inter-compared and particle losses due to different sampling lines were obtained and data were corrected accordingly. Measurements were made concurrently at the 3 different sites at similar time resolution (5 minutes interval at RP and BT; 10 minutes interval at MR).

The field study was conducted between 17-10-07 and 09-11-07, and approximately 7000 SMPS size distributions were measured. These size distributions were averaged over 6 hour intervals (00-06, 06-12, 12-18, 18-00) reducing their number from 20,000 to 259, which were subsequently normalised by their vector-length and cluster analysed. The Dunn-Index for the results of the K-means cluster analysis for different cluster numbers showed a clear maximum for 15 clusters, some of which belonged only to specific sampling sites and to specific time of the day. The intensive observations of aerosols, trace gases and boundary layer dynamics were used to quantify the variability in urban aerosols due to both chemical and meteorological processes. The 15 clusters were composed of unique particle size distributions, and they were analyzed along with the urban boundary layer (UBL) dynamics obtained with the lidar.

Different case studies are presented including:

1. A higher particle number concentrations of nano particles (<50nm) was observed at the tower (170m above the city of London) during days affected by higher turbulence, implying a clear transport of freshly emitted traffic related particles from the ground to the upper part of the UBL.

2. A more uniform particle size distributions along the 3 sites were observed during shallow UBL conditions, implying that the urban aerosols were mixed along the shallow UBL and so the tower site was more affected by local aerosol emissions.

3. Clear conditions of UBL decoupling between the ground sites and the tower site caused the particle size distributions between being different between the 2 conditions. The tower site was characterised by long range transport particle size distributions, whilst the ground sites one by more urban-like ones.

### ACKNOWLEDGEMENTS

This research was supported by the UK Natural Environment Research Council as part of the programme of the National Centre for Atmospheric Science. The authors are grateful also to the BOC Foundation for financial support of campaign expenses and to British Telecom and the Royal Parks for facilitating access to measurement sites.

## Remarkable dynamics of nanoparticle in the urban atmosphere

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Keywords: Urban Aerosol, Aerosol Size Distribution, Aerosol Evolution, SMPS, Ultrafine Aerosols

Nanoparticles emitted from road traffic are the largest source of respiratory exposure for the general public living in urban areas. It has been suggested that adverse health effects of airborne particles may scale with airborne particle number, which if correct, focuses attention on the nanoparticle (less than 100 nanometre) size range which dominate the number count in urban areas.

During the REPARTEE field campaigns held in London each for four weeks in October 2006 and September 2007, measurements of particle number concentrations were made using condensation particle counters, and number size distributions using Scanning Mobility Particle Sizers at sampling sites located in the centre of Regents Park (of the order of 700 metres from major highways), and at a height of 170 metres above ground level on the BT Tower (1.2 km horizontally from the Regents Park site). Additionally, information collected at the urban central background site at London, North Kensington, and the roadside sampling site of London Marylebone Road which has traffic flows of around 70,000 vehicles per day and provides the main southern boundary to Regents Park and runs between Regents Park and the BT Tower were used.

The average diurnal pattern of particle number count at all four sites clearly showed a gradient in number concentrations from Marylebone Road, peaking at around  $100 \times 10^3 \text{ cm}^{-3}$  to Regents Park (around  $38 \times 10^3 \text{ cm}^{-3}$ ), London, North Kensington ( $25 \times 10^3 \text{ cm}^{-3}$ ) and the BT Tower ( $9 \times 10^3 \text{ cm}^{-3}$ ). The high ratio in particle number concentrations between the ground-based sites and the BT Tower could not be explained by dispersion processes alone.

Further evidence on this phenomenon were derived from a comparison of particle size distributions at three sites (Figure 1).

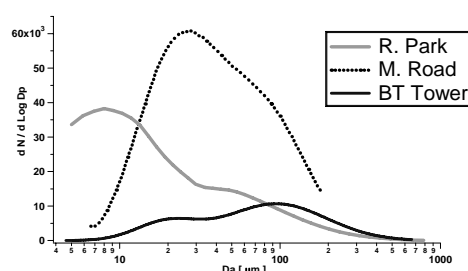


Figure 1. Average particle size distributions (mobility diameter, nm) at Marylebone Road, Regents Park and BT Tower.

The size distribution measured at Marylebone Road was typical of roadside and on-road number size distributions, peaking between 20 and 30 nm diameter. In contrast, data from the Regents Park site showed a mode which had shifted downwards to below 10 nm diameter together with some overall loss of area under the curve representing a loss of total particle number.

When a curve-fitting programme was used to disaggregate these size distributions into a number of log-normal distributions, the results suggested that even within the urban atmosphere, on distance scales of the order of 1 km and travel times of around 5 minutes upon moving away from major emissions sources very significant loss of the nanoparticle fraction is observed which manifests itself in a shift to smaller sizes within Regents Park and an almost complete loss of the sub-30 nanometre mode at the BT Tower site.

### ACKNOWLEDGEMENTS

The authors are grateful to British Telecom for allowing access to the BT Tower and to the Royal Parks for providing facilities at Regent's Park. Funding was provided by the Natural Environment Research Council and BOC Foundation.

## **REPARTEE-I and REPARTEE-II (Regent's Park and Tower Environmental Experiment)**

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Keywords: (Urban Aerosol, Aerosol Chemistry, Aerosol Evolution, Air Quality, Airborne Particles)

This project brought together NCAS (National Centre for Atmospheric Science) scientists to study atmospheric chemical processes, and particularly those affecting atmospheric aerosol, in London by using the following sampling platforms:

- the BT tower at an elevation of 170 metres above ground level.
- adjacent Regents Park where ground level measurements were made.
- Marylebone Road at roadside in the street canyon.

Two air sampling campaigns were carried out throughout the months of October 2006 and October/November 2007. The objectives of the two campaigns were:

1. To understand the fate of traffic-generated nano-particles in the urban atmosphere
2. To determine fluxes of trace gases and particles above central London
3. To use the vertical and horizontal separation of sampling sites to study the evolution of chemical composition and physical properties of particles
4. To study the chemical properties and formation mechanisms of major components of airborne particles (especially nitrogen-containing)

A wide range of measurements were taken including:

### REPARTEE I (2006)

- Particle and gas fluxes were measured at the elevated site (AMS, CPC, GRAEGOR, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub>)
- Real time chemical composition of aerosol by particle mass spectrometry at the park (AMS, ATOFMS).

- 24-hours size resolved PM chemical composition with MOUDI and Partisol at the park and at the tower.
- Size distribution of particulate matter with SMPS and APS in order to describe the evolution of the traffic component vertically and horizontally at the 3 sites.
- Fluorocarbon tracer sampler release from the park

### REPARTEE II (2007)

The REPARTEE I results added some more objectives, addressed with additional instrumentation deployed during the REPARTEE II:

- LIDAR, deployed near the road site in order to describe the atmospheric boundary-layer (ABL) structure.
- NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> CEAS system at the tower in order to elucidate the nitrate chemistry.
- Nano-SMPS at the tower in order to monitor the fate of the nano particles.

An overview of the 3 monitoring sites, including instrumentation used, method of aerosol sampling will be presented together with an overview of results.

### ACKNOWLEDGEMENTS

The authors are grateful to British Telecom for allowing access to the BT Tower and to the Royal Parks for providing facilities at Regent's Park. Funding was provided by the Natural Environment Research Council and BOC Foundation. The Doppler Lidar was provided by NERC FGAM.

## Physico-Chemical Aerosol Dispersion in Urban Environments

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Keywords: Aerosol Dynamics, Air Pollution, CFD, Chemical properties, Fluxes

The spatial heterogeneity of urban street canyons and the complex interplay of chemically, spatially and temporally varying ultrafine particle emission sources as a function of micrometeorological and meteorological factors represents a challenge to both computational fluid dynamical modelling approaches and field observations. Intensive measurement campaigns or networks generally have insufficient spatial resolution or temporal resolution respectively to adequately represent the entire vertical or horizontal spatial structure of aerosol and these must be informed by numerical dispersion modeling combined with realistic aerosol physico-chemical descriptions to be of benefit to epidemiological studies. Predictions of vertical and horizontal structure of aerosols in street canyons are therefore required to inform future directives regarding recommended sampling and monitoring protocols.

Here we compare first-order eddy viscosity turbulence closure CFD predictions with recent measurement results demonstrating the impact of different relative contributions of convective and turbulent diffusivities on aerosol distribution profiles at different locations within street canyons.

We describe preliminary results with a CFD model where we have incorporated more realistic aerosol processes such as condensation and coagulation by oxidation and condensation of hydrocarbon species. We examine how these processes influence the vertical and horizontal distributions of aerosol parameters.

From the dynamical perspective we investigate the different factors that influence the aerosol exchange velocity between street canyons and the urban boundary layer above. Both vertical turbulent fluxes as well as the fluxes due to mean flow are shown to contribute to the overall ventilation characteristics of a street canyon.

We then compare emission velocity structure within and above the canyon and compare these with observations, e.g. Longley et al. (2004). We then discuss these in context with tower based micrometeorological flux measurements that were obtained from the CITYFLUX and REPARTEE

studies, Martin et al. (2009).

Whilst undoubtedly crude these comparisons may be used as a starting point for linking street level concentrations to those measured above the urban roughness layer e.g. on large scale micrometeorological flux measurement towers as used in REPARTEE and CITYFLUX with potential for validating high resolution regional scale air quality models.

How such approaches can be used to facilitate parameterizations suitable for other modelling platforms such as those that are more appropriate to the epidemiological study domain still remains a challenge. Again as a starting point we discuss potential linkages with ultrafine aerosol affinity zones, Harris et al. (2009), which can be derived using Geographical Information Science tools (GISc) model techniques. These zones require city specific validation. While this can be achieved partly by traditional sampling networks coupled with intensive micrometeorological canyon flux observations, these are expensive. There is potential cost benefit therefore to using area averaged flux footprint databases, determined by long term large tower based micrometeorological measurement systems, to inform many of these modeling approaches.

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Harris, P., et al. (2009). Identification and verification of ultrafine particle affinity zones in urban neighbourhoods. NERC Environment and Human Health Programme Annual Science Day Conference & Workshop, Univ. Birmingham, February 2009

Longley, I.D., Gallagher, M.W., Dorsey, J.R., Flynn, M. (2004). A case-study of fine particle concentrations and fluxes measured in a busy street canyon in Manchester, *Atmospheric Environment*, 38 (22):3595-3603.

Martin, C., et al. (2009). Ultrafine particle fluxes above four major European cities. *Atmospheric Environment* (In Press ATMENV-D-08-00249R1).



## Lidar data analysis from REPARTEE II campaign

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Keywords: aerosol dynamics, meteorology, mixing layer, lidar, urban areas

The atmospheric boundary layer is multi-structured, and the presence of an urban surface below makes this structure more complex. The varying surface types present within an urban landscape can cause the formation of internal layers with differing turbulence regimes within. These different layers can have significant effects upon the vertical mixing of aerosol throughout the lower atmosphere both in terms of height and velocity. Doppler lidars are the ideal instrument for examining the structure of the boundary layer, as they give us information on both the location of aerosols within the layer and the turbulent motion taking place. A doppler lidar was deployed during the REPARTEE II campaign and the data gathered has been analysed in terms of the dynamics of the boundary layer, concentrating in particular upon the identification of different layers within the boundary layer and the effect these have upon transport of aerosols.

The REPARTEE project aimed to compare aerosol measurements made at the surface at Regent's Park, to measurements from the top of the BT Tower (at 190m), and thereby study the transport and transformation of aerosols within the layer. As part of the experiment, the UFAM doppler lidar operated continuously for three weeks between the 24th of October and the 14th of November 2007. It was positioned on the

Marylebone road near to Regent's Park, London.

Figure 1. below shows a time-height plot of lidar backscatter on a typical convective day during the REPARTEE campaign. Plotted on top of this are the mixing layer height, determined from measurements of the vertical velocity variance, and the heights of two different aerosol layers, determined from the backscatter. During the daytime, from 0900 to 1700, the mixing layer grows from the surface to the top of the boundary layer, indicating the depth of vertical mixing present due to convective turbulence. After 1700, the lack of surface heating causes the mixing layer depth to return to the surface. During the preceding night, from 0000 to 0900, although there is little convective mixing present, there is a distinct layer of aerosol adjacent to the surface, indicating a stably stratified nocturnal layer, with some mixing present due to shear turbulence.

The lidar measurements have also been compared to those taken by the sonic anemometer at the top of the BT Tower. At night-time, discrepancies between the levels of turbulence at this height can be interpreted as the presence of a stable layer forming over Regent's Park. This decoupling of the turbulence between the surface and aloft can be linked to the differing evolution of aerosol species measured at the two heights.

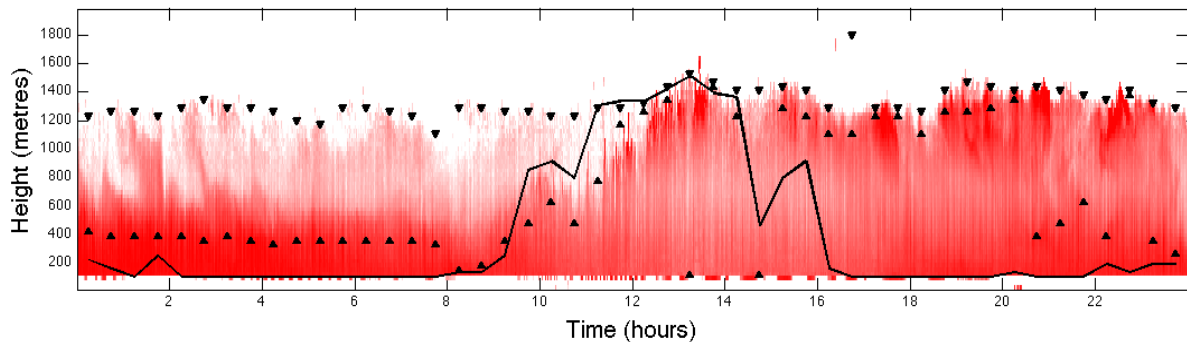


Figure 1: The backscatter detected by the lidar on the 6th of November, 2007 during the REPARTEE II campaign. Plotted on top are the heights of different aerosol layers as detected using the lidar measurements of backscatter (upward and downward pointing triangles) and the mixing layer height measured using the variance of the vertical velocity (solid line).

## Nitrate Dynamics in UK Urban Environments

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Keywords: Ammonium Nitrate, Anthropogenic Aerosol, Aerosol Mass Spectrometry, Urban Aerosols, Inorganics, .

Nitrate makes a significant contribution to the concentration of PM<sub>2.5</sub> and PM<sub>10</sub> with important implications for human health and regional climate forcing. This is particularly true for NW Europe, where large emissions of NH<sub>3</sub> and NO<sub>x</sub> combine with comparably low temperatures and high relative humidities to create conditions that favour the production of NH<sub>4</sub>NO<sub>3</sub>. Despite its importance, most atmospheric chemistry models are still not modelling NH<sub>4</sub>NO<sub>3</sub> very well, indicating that dynamics are still not represented correctly. In addition, due to its changing equilibrium, there are processes which operated at a sub-grid scale and are therefore difficult to simulate.

In this presentation we review new evidence on nitrate dynamics in urban environments, drawing on data from recent urban field studies, mainly, but not exclusively, in the UK. This new look is enabled through the use of new measurement technology such as Aerosol Mass Spectrometry (AMS), urban eddy-covariance flux measurements of aerosol chemical compounds and long-term nitrate measurements.

We quantify the relative contribution NH<sub>4</sub>NO<sub>3</sub> to the UK aerosol, reviewing the existing UK AMS database and data from UK and European denuder/filter-pack networks.

Paired long-term measurements of aerosol concentrations in and outside of two UK urban areas (London & Edinburgh; Tang *et al.*, 2008), have provided information on the urban NO<sub>3</sub><sup>-</sup> increment. The measurements indicate that, on average:

$$\text{NO}_3^-(\text{urban}) = 1.13 \times \text{NO}_3^-(\text{rural}) + 0.58 \mu\text{g m}^{-3},$$

with somewhat larger increments during the winter months than during summer.

Measurements of the size-distributions of sub-micron non-refractory NO<sub>3</sub><sup>-</sup> by aerosol mass spectrometry frequently show periods of a NO<sub>3</sub><sup>-</sup> size mode in the range 100 to 300 nm, in addition to the accumulation mode at 300 to 800 nm. This suggests that NO<sub>3</sub><sup>-</sup> is formed by condensation on the combustion mode which is prevalent near traffic sources. The fine NO<sub>3</sub><sup>-</sup> mode is sporadically observed, and appears to correlate with cold, humid conditions and atmospheric inversions.

The role of urban areas in producing NH<sub>4</sub>NO<sub>3</sub> is further supported by the growing database of aerosol chemical compounds above urban areas, by aerosol mass spectrometry (e.g. Nemitz *et al.*, 2008), which suggests emission of NO<sub>3</sub><sup>-</sup> from most cities, which is nevertheless highly variable between days (unlike the emission of organic aerosol).

Vertical gradient measurements above the city centre of London during the REPARTEE campaign (comparing measurements on the Telecom tower at 165 m with ground-based urban background measurements) show higher NO<sub>3</sub><sup>-</sup> concentrations on the tower, possibly due to colder temperatures at higher heights shifting the gas/aerosol equilibrium towards the aerosol phase.

We also present evidence that the fate of NH<sub>4</sub>NO<sub>3</sub> is affected by its dissociation potential. In warm conditions, NH<sub>4</sub>NO<sub>3</sub> volatilises during the deposition process to semi-natural vegetation near the ground, where temperatures are raised and concentrations of NH<sub>3</sub> and HNO<sub>3</sub> lowered due to deposition. This greatly increases the effective deposition rate of NH<sub>4</sub>NO<sub>3</sub> aerosol and greatly decreases its atmospheric lifetime. Since this volatilisation near the ground cannot be resolved by current CTMs, it is suggested that effective deposition rates need to be incorporated into models to account for this effect.

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Nemitz, E.; Jimenez, J.L.; Huffman, J.A.; Canagaratna, M.R.; Worsnop, D.R.; Guenther, A.B. (2008). *Aerosol Science and Technology*, **42** (8). 636-657.

Tang, Y. S.; Sutton, M. A.; Simmons, I.; Love, L.; Vogt, E.; van Dijk, N.; Cape, J. N.; Smith, R. I.; Armas-Sanchez, E.; Lawrence, H.; Hayman, G. (2007). Monitoring of nitric acid, particulate nitrate and other species in the UK-2006. Interim report under the UK Acid Deposition Monitoring Network to NETCEN/DEFRA. Edinburgh, Centre for Ecology and Hydrology, 26pp.