Quantification of airborne road-side pollution carbon nanoparticles

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Abstract. Roadside diesel particulate matter (DPM) has been collected using a P-Trak particle counter with modified inlet filter. The P-Trak monitor assesses ultrafine particle number in real-time rather than accumulated PM mass over a period of time, which is important for DPM where the particles are often <100nm in size. Collected pollution particulate matter was analysed by SEM and TEM, quantifying particle size, morphology and size distribution. The primary carbon nanoparticles form complex fractal aggregates with open porous morphologies and evidence of secondary carbon deposition. For the chosen collection sites, occasional but significantly larger mineral and fibrous particles were identified. The assessment of airborne particles by mass collection (TEOM), particle-number (P-Trak) and TEM methods is discussed.

1. Introduction

Airborne particles have potential to cause significant detrimental impact on human health, with the ability to penetrate deep into the human lungs depending on their size. Airborne particles come from a range of manmade and natural sources, with particular concern focusing on the range of $PM_{2.5}$ and $PM_{1.0}$ particulate matter that are generated by the burning of diesel fuels [1]. The World Health Organization (WHO) states that diesel emissions are carcinogenic to humans based on 'sufficient evidence that exposure is associated with an increased risk for lung cancer' [2]. The key outdoor air pollutants are ozone (O_3), nitrogen oxides (NO_x), particulate matter (PM) and sulphur dioxide (SO_2), causing 3.7 million premature deaths in 2012 [2].

There is clear evidence that airborne carbon-based diesel particulate matter (DPM) is concentrated in the vicinity of roads within our cities [3-5]. A variety of detection systems have been used to measure nanoparticle presence and exposure, including the scanning mobility particle sizer (SMPS) [6], aerosol mass spectrometer (AMS) [7], and ultrafine particle counter (UPC) [8]. Each method defines a different particle "equivalent diameter" based on the physical method of counting the number and sizes of the particles. The analysis of airborne particles by scanning and transmission electron microscopy (SEM, TEM) based methods [9, 10] is also important, to form a link between particle mass/number monitoring, and particle identity, since different particle chemistries and morphologies can exhibit different biological activity. The present study analyses the collection of airborne particles by UPC and evaluates particle size, morphology and size distributions using comparative SEM-based and TEM-based methods.

2. Collection of airborne road-side pollution

Airborne particles were collected using a TSI P-Trak Ultrafine Particle Counter (UPC) 8525. This instrument is based on the principle of condensation particle counting, able to detect particle concentrations up to $5x10^5$ particles/cm^3 with particle diameters from 20nm to 1μm at a constant total flow rate of 700cm^3/min. Samples were collected concurrently with particle counting using TEM collection grids attached to the UPC inlet screen. An advantage of this method is that particles are collected directly onto the TEM grids without further manipulation.

Two holey carbon films on 300 Mesh Copper TEM Grids (AGS147, Agar Scientific) were welded to a coarse support mesh using silver conductive paint. Measurements were performed on April 29 2015 between 8:00AM and 9:30AM on the busy University of Sheffield roundabout where three major roads intersect. Sampling times were 15 minutes and 60 minutes, in order to evaluate time dependant particle effects. A tapered element oscillating microbalance (TEOM) teflon-coated glass fiber filter was used as reference to compare DPM agglomerates. The TEOM is located in the Sheffield City Council air pollution monitoring Station in Devonshire Green Park.

Transmission electron microscopy (JEOL JEM 3010) was used to evaluate size and morphology of the collected airborne aerosol particles. Scanning electron microscopy (FEI Inspect F) was used to evaluate particle distribution and characterise big agglomerates. The TEOM filter was gold-coated for 2 minutes at 15mA (Emscope, Quorum Technologies) to inhibit charging.

3. Characterisation of airborne pollution particulates

Figure 1 illustrates the types of particles collected in TEOM and UPC measurements. For both collection methods particles captured were dominated by carbon aggregates comprised of ~20nm diameter primary carbon nanoparticles (figure 1(b)). The macroscopic DPM agglomerates observed in the TEOM micrographs are formed due to gravitational sedimentation under controlled environmental conditions. Occasional larger particles were captured (arrowed figure 1(a)). Figure 2 illustrates some $PM_{2.5}$ and PM_{10} particles with complex shapes of both organic and man-made origin, that were observed decorated with smaller $PM_{1.0}$ particles.

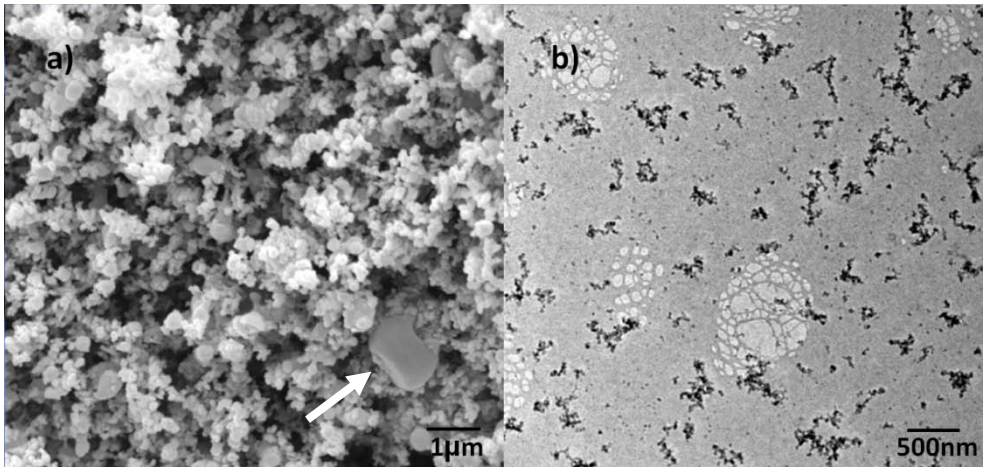

Figure 1. (a) SEM image of airborne pollution accumulated on a TEOM filter.
(b) TEM image of typical DPM particles collected by P-Trak UPC.

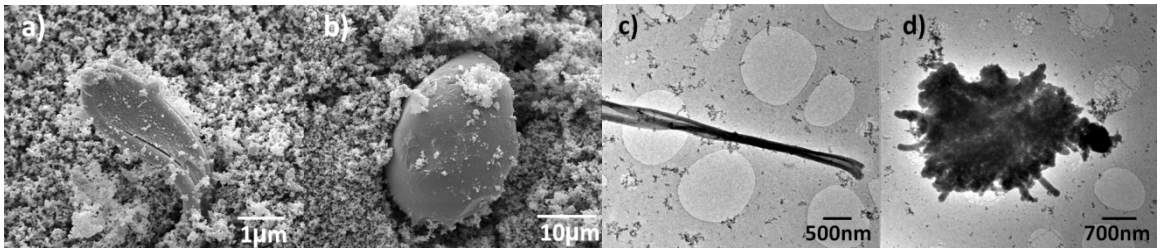

Figure 2. Larger $PM_{2.5}$ and PM_{10} pollution particles collected including (a,b) planar and ovalate particles, (c) nanoporous fibres, (d) fibre aggregates.

Individual DPM particles collected by P-Trak have a fractal-like morphology of agglomerated carbonaceous primary spherules [12]. In TEM projection the DPM aggregates appear well adhered to the holey carbon substrate (figure 3(a)), however their complex 3D fractal morphology means that they are frequently only attached at a few locations. The irregular 3D shapes can be characterised by calculating their radius of gyration taking into consideration the diameter and number of primary spherules of the aggregate [12].

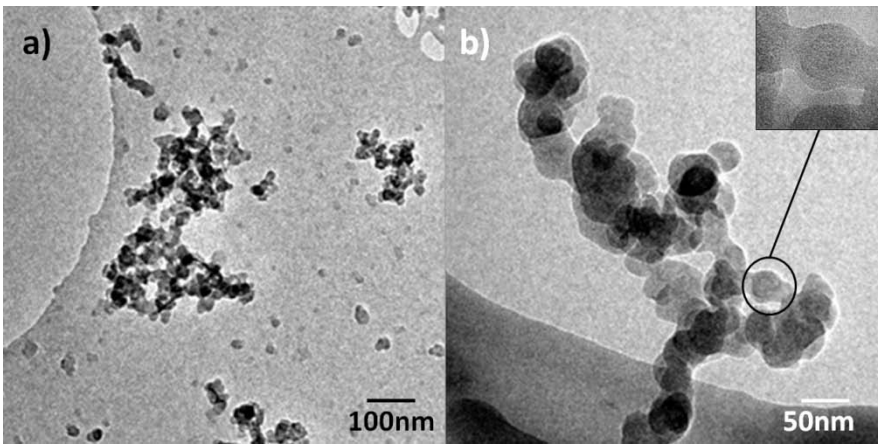

Figure 3. (a, b) Fractal morphologies of diesel soot particles comprised of nanoparticle aggregates with some evidence of secondary carbon layers (b).

To evaluate the number and size of DPM aggregates, the projected area of particles was measured by image analysis and an "equivalent diameter" calculated from a circle with the same area [11]. This method is accurate for spherical-like particles but does not accurately represent 3D fractal-like aggregates which can have very different projected cross-sections depending on imaging direction. Figure 4 shows the particle size distribution of 15 min and 60 min samples, analysed across the same total area of substrate by this methodology. It can be seen that more than 80% of the analysed particles were between the range of 18 and 24 nm which correspond to individual primary spherical particles. Larger aggregates represent less than 20% of particle number, but contribute a more significant percentage of particle mass [12].

Comparing the samples collected for 15 and 60 minutes, a marked variation in either of the projected density of particles or in their size distribution was not observed. This indicates that particles are not accumulating on the TEM grid with time, or merging as larger aggregates on the grid. This behaviour is consistent with a dynamical process whereby particles collide with the holey carbon TEM grid, a fraction adhering to it, but simultaneously a fraction of particles on the grid being dislodged in the incident airstream and being removed (figure 4(b)). This generates a steady state flow system where there is no net mass accumulation between 15 and 60 minute collection duration and a turbulent air flow as particles are observed in both sides of the grid.

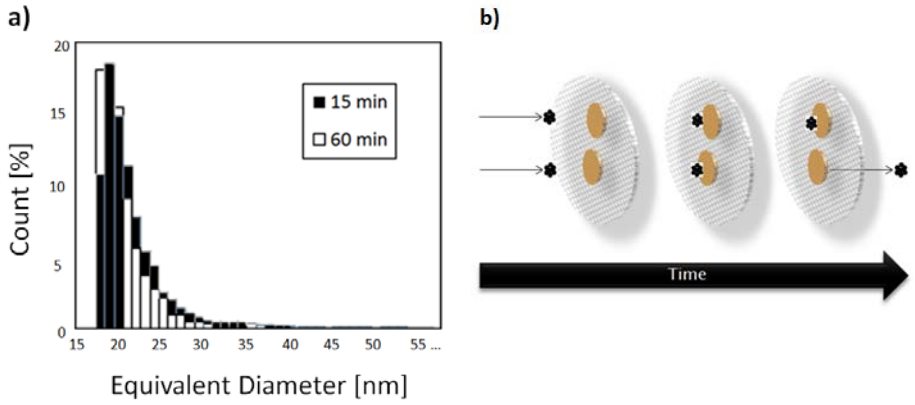

Figure 4. (a) Pollution particle size distribution of 15 min and 60 min samples collected by P-Trak. (b) Schematic of dynamical aerosol particle adhesion and removal on the TEM collection grids mounted on the P-Trak inlet screen

4. Conclusions

Airborne nanoparticles were collected directly into TEM grids using a commercial P-Trak UPC with modified inlet tube for further TEM and SEM analysis. Existing analysis methods assume DPM particles to be spherical [11] but they misrepresent larger soot aggregates which have fractal morphology. For 15min and 60min collection times on holey carbon TEM grids, there was no accumulation of DPM soot as a function of time. This is consistent with a steady state scenario whereby weakly bonded particles (limited contact area with the carbon film due to their fractal morphology) are constantly coming on and off the TEM grids. In the UPC the airflow may be turbulent as air passes through the holey carbon film and the coarse grid, and indeed particles were detected on both sides of the TEM collection grid. By comparison, in the TEOM method particles are collected in a slow gravitational airflow to assess mass accumulation. This study indicates the importance of local airflow to the dynamics of pollution particle adhesion to the collection media during aerosol sampling and assessment.

5. Acknowledgements

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6. References

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