



Comparative study of single particle characterisation by Transmission Electron Microscopy and time-of-flight aerosol mass spectrometry in the London atmosphere

Steve Smith^{a,*}, Mike Ward^b, Ray Lin^b, Rik Brydson^b, Manuel Dall'Osto^{c,d}, Roy M. Harrison^{c,1}

^a Department of Earth Sciences, Royal Holloway, University of London, Egham TW20 0EX, United Kingdom

^b Institute for Materials Research, SPEME, University of Leeds, Leeds LS2 9JT, United Kingdom

^c National Centre for Atmospheric Science, Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

^d Institute of Environmental Assessment and Water Research, Spanish Research Council (IDAEA-CSIC), c/Jordi Girona 18-26, 08034 Barcelona, Spain

HIGHLIGHTS

- ▶ Size-fractionated particles were collected at BT Tower and Regents Park, London.
- ▶ Characterization of particles was by TEM (EDX) and ATOFMS in real-time.
- ▶ TEM identified 8 types common to both sites with soot-like particles predominating.
- ▶ ATOFMS identified 13 types at Regents Park but only 3 were common to the 8 by TEM.
- ▶ TEM fails to identify semi-volatiles but traces involatile particles effectively.

ARTICLE INFO

Article history:

Received 17 January 2012

Received in revised form

7 August 2012

Accepted 8 August 2012

Keywords:

Transmission Electron Microscope

ATOFMS

Airborne particles

Particulate matter

Atmospheric aerosol

ABSTRACT

Size fractionated airborne particle samples were collected from the top of the BT Tower and a ground-based site in Regents Park in London by deploying MOUDI instruments at the two locations. Particles were examined by Transmission Electron Microscope (TEM), Energy Dispersive X-Ray Analysis (EDX) and selected area electron diffraction patterns to determine the morphology, crystallinity and composition of individual particles in aggregated and non-aggregated forms. Eight different types of particles were observed which were common both to the ground-based location and some 160 m above the conurbation of London at the top of the BT Tower. Of these different types, amorphous carbonaceous aggregates (soot-like) containing C and O and often extending to the inclusion of Ca, K and Fe were the most common type of particles that occurred across all stages of the impactors but were most common in the fractions <1.2 μm. Other types of particles included beam-sensitive sulphur-rich particles containing Na and Cl that were present in crystalline and amorphous forms. Iron and titanium were common elements in other types of particles. Concurrent ATOFMS measurements were taken at the Regents Park site and 13 particle types were found. An intercomparison of the two techniques found three types of particle (out of eight) identified by the TEM, which had analogues (but not direct equivalents) in the ATOFMS clusters. Many of the particle types identified by the ATOFMS are vacuum-volatile (e.g. nitrates) and are therefore not seen by the TEM. The relative strengths and weaknesses of the two techniques are considered and it is concluded that both have major weaknesses but that they tend to complement one another.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

It is widely acknowledged that airborne particle matter (APM) is damaging to health. Epidemiological studies have established associations between the mass concentration of respirable particles in urban areas (PM₁₀ and PM_{2.5}; aerodynamic diameter <10 μm and <2.5 μm respectively) and pulmonary and cardiovascular diseases, with chronic effects associated with the fine (PM_{2.5})

* Corresponding author.

E-mail address: steve.smith@es.rhul.ac.uk (S. Smith).

¹ Also at: Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah 21589, Saudi Arabia.

fraction of particulate matter (Pope et al., 2002; Dockery et al., 1993; Health Effects Institute, 2000; Pope et al., 2004; WHO, 2004). Combustion sources of particles are considered to be particularly important for the health effects (Laden et al., 2000; WHO, 2004; Peng et al., 2009) and toxicological studies have shown that for particles of similar composition, toxicity may increase as particle size decreases and nano-sized particles are widely regarded as the most toxic (Duffin et al., 2002). As the health implications of particles with size dimensions in the nanometre-range have become apparent (Atkinson et al., 2010), it is important to examine the physical and chemical characteristics of particles in this size range.

Bulk analysis of the atmospheric aerosol typically concerns the PM₁₀ or PM_{2.5} fraction and it is well established that the major chemical components are elemental carbon, organic compounds, ammonium sulphate, ammonium nitrate, metal-rich coarse dusts, sea salt and bound water (Harrison et al., 2003). Bulk analyses do not provide direct information on the physical and chemical characteristics of individual, small clusters or agglomerates of particles. Moreover the small mass of the sub-micron fraction is an analytical challenge for most types of methods of bulk analyses.

Transmission Electron Microscopy (TEM) is a powerful technique for characterizing size and morphology of particles in the micron and sub-micron size range. The associated spectroscopic techniques of Energy Dispersive X-ray (EDX) analysis and selected area electron diffraction provide information on the chemical composition and crystal structure of individual particles; examples include Calvert et al. (2003), Bérubé et al. (1999), Pósfai et al. (1994), Murr and Bang (2003), Murr and Garza (2009) and Chen et al. (2006).

Aerosol time-of-flight mass spectrometry (ATOFMS) is also a powerful technique for characterizing individual particles in real time down to 100 nm. Organic and inorganic aerosol material are desorbed and ionized from single particles by an intense laser pulse, generating positive and negative ions, which are subsequently analysed by a dual polarity time-of-flight mass spectrometer. The classification of several different particle types is possible through knowledge of their chemical fingerprints (Gross et al., 2000; Silva and Prather, 2000).

The Regents Park and Tower Environmental Experiment (REPARTEE) comprised two measurement campaigns in London in October 2006 and October/November 2007 and included a wide range of measurements of airborne particle metrics and chemical compositions; Harrison et al., 2012 gives an overview of REPARTEE. As part of the REPARTEE experiment, a TEM study was undertaken of samples of particulate matter, which had been collected at two sites in London, aloft on the BT Tower (160 m) and at a nearby ground-level location in Regents Park. An ATOFMS instrument ran over the same period at Regents Park. This paper is concerned with inter-comparing the information derived from the two methods.

2. Methods

Sampling locations were the BT tower at an elevation of 160 m above ground level and Regents Park where ground level measurements were made between 4th and 23rd October 2006. Regents Park is located in the northern part of central London and adjacent to BT tower. More information about the sites can be found in Harrison et al. (2012).

2.1. MOUDI

Samples were collected on each of the 9 impactor stages of MOUDI (Micro-Orifice Uniform Deposit Impactor, model 110, MSP Corp) instruments deployed at the two sampling locations.

Sampling flow was supplied by a Gast twin piston pump. The cut-off parameters of the MOUDI stages were adjusted according to the actual flow rate of 25.5 L min⁻¹, and the 50% cut-points for particle aerodynamic diameter for each stage were: 1, >21 µm; 2, 11.5–21 µm; 3, 7.2–11.5 µm; 4, 3.7–7.2 µm; 5, 2.2–3.7 µm; 6, 1.2–2.2 µm; 7, 0.7–1.2 µm; 8, 0.4–0.7 µm; 9, 0.2–0.4 µm. The fractionated particles at each MOUDI stage were collected on Teflon filters previously treated with silicone grease to avoid particle bounce.

Samples for TEM analysis were obtained by two methods: (1) Particles were collected directly onto TEM grids (holey carbon film on 400 mesh copper or gold grids, Agar Scientific) affixed to the surface of the PTFE filters on each stage of the impactor. The impactors were operated for 120 min in between standard 48-h operation of the instruments. (2) Quarter sections of PTFE filters with deposits collected for a set 48-h period were obtained. Approximately 1 cm², from the corner of the quarter segment supplied was immersed in 0.5 ml of acetone in a sealed container and sonicated for 30 min. Following this, 5 drops of the dispersion were drop-cast onto a standard TEM specimen support grid (holey carbon film supported on 400 mesh copper grids, Agar Scientific). Once dried the grid was placed into the TEM and examined.

2.2. Transmission Electron Microscopy

Transmission Electron Microscopy was conducted using a Philips FEI CM200 FEG TEM STEM operated at 197 kV equipped with an Oxford Instruments UTW EDX detector and a Gatan GIF200 Imaging Filter. For both methods of preparing particles, 27 particles were studied for each sample. A specific sampling method was adopted which attempted to remove bias in the choice of particles analysed. Particles were selected by starting in the central grid square, and picking a particle from the centre, the top right, centre right, bottom right, and clockwise around to the top left of the grid square. The particles were selected by going to low magnification mode in the microscope, centring the region of interest within the grid square (e.g. top right, centre right, etc.) on the viewing screen, and then increasing the magnification until particles were visible; the particle closest to the centre of the screen was chosen. This method resulted in 9 particles being examined for each grid square. For each sample, two other grid squares were chosen by moving 5 squares to the right and 5 squares down, from the centre grid square respectively. This meant that for each sample, 3 grid squares were studied and 27 particles in total.

For each particle, a bright field TEM image was recorded along with an EDX spectrum. The crystallinity of the particles was also examined by observing the selected area electron diffraction pattern.

2.3. ATOFMS

A TSI model 3800 ATOFMS was used, fitted with a model 3800-100 aerodynamic focussing lens. Ambient aerosol is focused into a narrow particle beam for sizes between 100 nm and 3 µm as ambient air is drawn in by the vacuum in the instrument. Using a 2-laser velocimeter, particle sizes are determined from particle velocity after acceleration into the vacuum. In addition, the light scattered by particles is used to trigger a pulsed high power desorption and ionization laser ($\lambda = 266$ nm, 1 mJ pulse⁻¹) which evaporates and ionizes the particle in the centre of the ion source of a bipolar reflectron ToFMS. Bipolar mass spectra of individual aerosol particles are obtained giving positive ion spectra of cations such as metal ions, ammonium and carbon-containing clusters and negative ion spectra showing carbon-containing clusters, anions like sulfate, phosphate, nitrate as well as certain organic species.

The intensities of the mass spectral peaks are qualitative as they are not directly proportional to the component mass but are dependent on the particle matrix, the coupling between the laser and the particle and the shot to shot variability of the laser. The ATOFMS provides quantitative information on particle number as a function of composition, which is used as a basis for identifying particle types and provides a measure of their abundance in the atmosphere.

The ATOFMS was deployed at Regent's Park for 19 days, between 04/10/06 at 17:00 and 22/10/06 at 23:00. In total 153,595 particles were captured by the instrument and positive and negative mass spectra of each one were recorded. These data were processed using YAADA (Yet Another ATOFMS Data Analyzer) and single particle mass spectra were grouped with Adaptive Resonance Theory neural network, ART-2a (Song et al., 1999), further details of data processing can be found in Dall'Osto et al. (2009a,b). Initially 306 clusters were found and further analysis revealed that many of these had similar characteristics and could be merged. By classifying in respect of temporal trends, size distributions and mass spectra, the clusters were reduced to 15 different particle types that were used as a basis for comparison in this study.

3. Results

The TEM samples for this study were collected between 1130 and 1330 on 13th October 2006. This day was characterised by relatively low pollutant concentrations – sulphate 1.4 ± 0.6 and $1.8 \pm 0.4 \mu\text{g m}^{-3}$, nitrate 1.6 ± 0.8 and 1.2 ± 0.7 , organic carbon 5.5 ± 2.2 and 5.3 ± 1.6 at the BT Tower and Regents Park sites respectively. Elemental carbon at the Park presented an average concentration of $4.2 \pm 1.6 \mu\text{g m}^{-3}$. During this period in the middle of the day, there was typically good atmospheric coupling between the two sites (Barlow et al., 2011).

3.1. Transmission Electron Microscope

The two methods of particle collection for the TEM study were envisaged to fulfil complementary roles, in that collection directly onto TEM grids for 120 min enabled a direct means of collecting particles with minimal impaction of one upon another, although it is acknowledged that particles would be subject to bounce-off processes or break-up of particles on impact to the grids. The objective of the second method in which particles were abstracted from a sub-section of a PTFE filter was to obtain a more representative aerosol sample covering the 48-h sampling period of the MOUDI instruments. However it is acknowledged that this type of sample preparation has limitations in terms of the efficiency of particle extraction from the filters and the possibility of chemical and physical alteration of particles during the preparation process. We contend from the results presented below that chemical and physical alteration had a significant influence on particle morphology and composition such that we restricted the comparison between TEM and ATOFMS to the period of collecting directly onto TEM grids.

Particles were classified according to Lin (2005; Supplemental Material, Figure S1) and analysed particles were placed into one of 8 distinct classes on the basis of their state of aggregation, their crystallinity and their composition (metal or non-metal). An aggregate was defined as a particle of five or more particles. A summary of the physical and chemical characteristics of particles collected on TEM grids is given in Fig. 1a (BT tower) and b (Regents Park RP); 8 particle types were common to both locations. Fig. 2 shows examples of the images and EDX spectra (see also Supplemental Material, Figure S2) and the different types are summarised below:

- (1) **Carbonaceous (non-metal).** Amorphous carbonaceous aggregates composed of spherules, typical of soot and which appear to be solely composed of either C, C with O or C with O and Si. They occurred on all impactor stages and at both locations, but the striking feature is their dominance on stages 7 (0.7–1.2 μm), 8 (0.4–0.7 μm) and 9 (0.2–0.4 μm) of the impactor; a range overlapping well with the size range of the ATOFMS measurements.
- (2) **Carbonaceous (metal contained).** Very similar amorphous carbonaceous aggregates to the first type but containing metals, commonly K, Ca, Fe and occasionally Cr.
- (3) **Na, Cl, S and K based particle.** Typically mixed-element non-aggregate particles, mainly consisting of Na, Cl, S and K in amorphous or crystalline forms, although crystalline forms were more common. This type of particle was most common on the 6th stage (1.2–2.2 μm) of the impactors and on the stages either side. Most of these sulphur-containing particles were electron beam sensitive and damaged relatively easily. This was observed as a rapid change in morphology and the appearance of moving pores within a particle. It is likely that these particles include soluble sulphate species such as $(\text{NH}_4)_2\text{SO}_4$ and related species (Posfai et al., 1994) as well as sodium chloride.
- (4) **Clay-type minerals.** Non-aggregated crystalline particles rich in both Si and Al.
- (5) **Fe based.** Iron occurs in a number of different forms of particle, including amorphous soot aggregates noted above. Crystalline aggregates containing Fe and O with traces of Si, S, K, Ca and Ti were observed as well as crystalline non-aggregates of Fe and O and with traces of Si and Ca. It is likely that these are morphologically different types of iron oxides.
- (6) **Ca based.** Ca-rich particles were found in both amorphous and crystalline forms. They included crystalline aggregates with strong Ca, O and C peaks together with traces of Si, Na and Al, indicating a mixture of substances, typical of soil-derived CaCO_3 and clay minerals.
- (7) **Sn based.** Non-aggregated, crystalline particles.
- (8) **Ti based.** TiO_2 particles were non-aggregates and crystalline and they were observed in two morphological forms; rounded cubical or nodular structures and needle-like forms.
- (9) Additionally, Pb-, Ag-, and graphite particles were observed at the BT Tower location.

Examination of particles extracted from PTFE filters in acetone revealed a different picture for the carbonaceous particles (Supplemental Material, Figure S3). There were many amorphous carbon particles but in contrast to the soot-type aggregates described above, they tended to be non-aggregated or small aggregates of more diffuse particles or they were observed to be nodular, smoother and more compact aggregates in appearance. Many had the same or very similar EDX profiles as the soot-type aggregates with C, O, Si the common elements but there were also morphologically similar particles that had multi-element spectra. It is possible that these particles were derived from amorphous carbon aggregates and the procedure of abstracting particles from filter substrates into a dispersion and transferring them to TEM grids could have been responsible for disaggregating the fractal units producing both individual particles and smaller aggregates of particles. Colbeck et al. (1990) have shown how combustion-generated aggregates tend to collapse to more compact structures when exposed to high relative humidities. Immersion in acetone, a polar aprotic solvent, probably has the same effect. The other types of particles listed above were less evident, although titanium-rich particles were common in all the samples. These were crystalline but as noted above they were of two distinct forms. One has a characteristic rounded cubic or

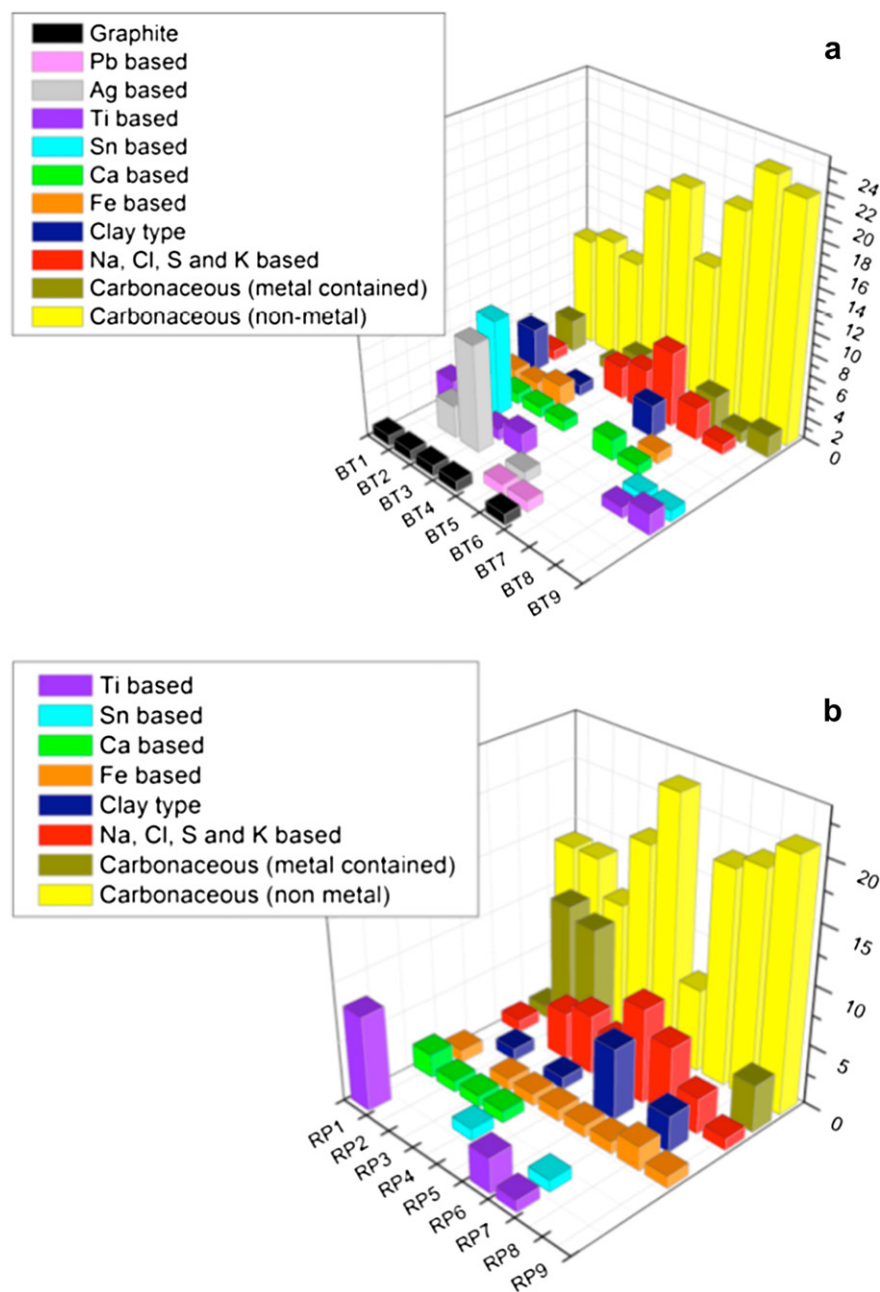


Fig. 1. The number of each type of particle observed on each of the 9 impactor stages of the MOUDI instruments at (a) the BT Tower and (b) Regents Park.

nodular crystal morphology, which often occurs in small clusters and they have been reported in the other studies and the other is needle-like in shape. Because of the uncertainties of the provenance of the particles abstracted from PTFE filters, it was decided to restrict the comparison with ATOFMS data to the short overlap period of the two hours of direct sampling directly onto TEM grids.

3.2. ATOFMS

During the REPAREE I field study 15 particle clusters were found. Of these, the 3 main clusters were associated with nitrate and have been discussed in Dall'Osto et al. (2009a). Twelve of the 15 clusters contained mass spectral peaks characteristic of organic containing particles, accounting for 83.7% of the total particles classified. Two specific ATOFMS clusters associated with secondary

organic aerosol production during a fog event have already been discussed in Dall'Osto et al. (2009b; Supplemental Material, Table S1). Additionally, four particle types postulated to be due to locally generated aerosols, independent of the air mass type advected into London (Ca-EC, Na-EC-OC, OC and SOA-PAH) are reported by Dall'Osto and Harrison (2012). Of these 15 particle types, 13 were encountered in the 2 h of this intercomparison (1130–1330, 13th October 2006). Particle types PAH and Na-EC-OC were not found during this study. The majority of particles detected with ATOFMS (>90%) comprise:

- Nitrate particles (41% of total particles) occurred in two distinct clusters, the first one appeared to be locally produced in urban locations during night-time and particles were generally smaller than 300 nm, whilst the second one was associated

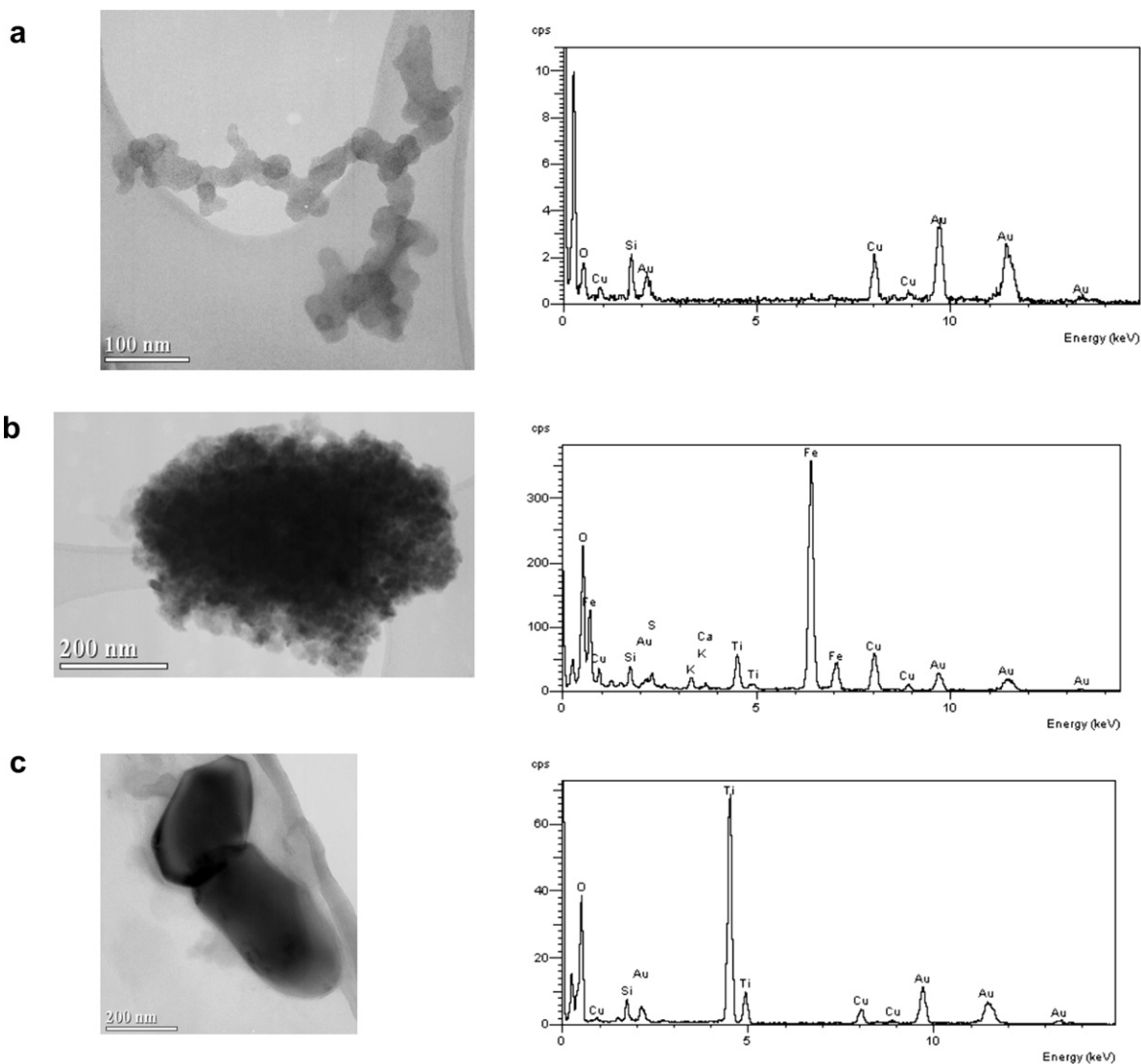


Fig. 2. Examples of Bright Field Images and EDX spectra of the different types of particulates observed at BT Tower and Regents Park (Cu and Au peaks are due to the type of TEM grid): a Carbonaceous; b Fe based; c Ti based particles.

with a regionally transported aerosol from continental Europe with larger particles of around 600 nm. Nitrate in both clusters was internally mixed with sulphate, ammonium, elemental and organic carbon.

- Ca-EC and OC (23%) were found mainly during morning rush hour traffic and correlated with primary organic aerosol. These primary organic aerosol ATOFMS classes, as well as a SOA-PAH cluster, are discussed in [Dall'Osto and Harrison \(2012\)](#).
- An Fe particle cluster (1.4%) mainly <1 μm in diameter, containing ^{54}Fe and ^{56}Fe was internally mixed with sodium, nitrate, sulphate and elemental carbon. The Fe cluster correlated with LRT nitrate. In contrast, previous ATOFMS studies found this type of particle was mainly associated a coarser mode and attributed to local dust.
- NaCl (19%). Two sub-classes were identified, NaCl (18%) and an aged NaCl (1%), which was associated with nitrate and indicative of NaCl reacting with HNO_3 forming $\text{NaNO}_3 \cdot \text{HCl}$.
- Fog event particles (9%). The latter part of a fog event coincided with the day of sampling, distinguished by the presence of hydroxymethanesulphonate (HMS), and the generation of an inorganic and organic secondary aerosol.

4. Discussion

4.1. TEM analysis

Other studies have reported similar morphologies and EDX spectra of carbonaceous particles to that found in this study (Supplemental Material Table S2). They include diesel soot with C and Si and C, O and Si signatures ([Wentzel et al., 2003](#); [Bérubé et al., 1999](#)), carbonaceous aggregates in samples from Greenland ice sheet ([Esquivel and Murr, 2004](#)), ambient particles in Lexington Kentucky ([Chen et al., 2006](#)), Mexico City ([Johnson et al., 2005](#)) and Norway ([Kocbach et al., 2005](#)) and nucleation particles from diesel combustion ([Kirchner et al., 2009](#)). [Kirchner et al., 2009](#) suggested that the Si signal is an artifact from the EDX detector and cite [Williams and Carter \(1996\)](#) in support of this observation. Inclusion of S is thought to indicate combustion of fuels containing sulphur ([Chen et al., 2006](#); [Bérubé et al., 1999](#); [Kirchner et al., 2009](#)). [Bérubé et al. \(1999\)](#) also observed aggregates containing P and Ca after a few minutes of engine running time which were associated with lubricant combustion. In Norway ([Kocbach et al., 2005](#)) at a location dominated by wood smoke, S and K were more dominant than Si

and Ca whereas at a vehicle dominated location Si and Ca were more prominent. Johnson et al. (2005) suggested that carbonaceous aggregates with C, O and small S peaks were indicative of fresh traffic emissions, whereas inclusions of K, Si with more prominent presence of S and to a lesser extent Fe, Na and P originated from different sources and demonstrated extensive particle mixing. In addition, tyre wear and brake dusts include carbonaceous particles. It is reported that tyre wear particles have a bimodal distribution with one mode in the supramicron size range and the other one in the sub-micron range whilst brake dust has an aerodynamic diameter of around 3 μm (Gietl et al., 2010). Elemental composition of brake and tyre dust can include Al and Si with traces of Fe, S and Zn (Adachi and Tainosho, 2004). Gualtieri et al. (2005) in an experimentally generated sample of tyre tread, observed that Sn, S and Si were the diagnostic elements.

Fe occurred in different types of particle, ranging from minor inclusions in amorphous carbonaceous aggregates to being the dominant element with oxygen in crystalline structures indicative of iron oxides. The significance of this is that Fe through its oxidation states of Fe^{2+} and Fe^{3+} is widely considered as a strong candidate for generating reactive oxygen species (ROS) and in turn accounting for much if not all of the toxicity of airborne particle matter. The forms and structural characteristics of Fe species in particles need further attention and clearly TEM can play an important role in this respect, particularly the use of EELS which could identify $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in individual particles (Calvert et al., 2005).

As reported in other TEM studies, Ti-rich particles are common and are thought to have both natural and anthropogenic origins, that include widespread use of Ti in the paint, cosmetics and pharmaceutical industries (Pósfai et al., 1994; Murr and Bang, 2003; Murr and Garza, 2009; Chen et al., 2006). Ti-rich particles of two different morphologies were observed, one was the commonly observed nodular crystalline form and the other was a needle-like structure. Kapp et al. (2004) generated a batch of ultrafine crystals of TiO_2 by a spark generator system and observed that about 7% were in a needle-like form and the rest were round/oval shaped crystals. Schulz et al. (2002) examined dermal absorption of three types of TiO_2 formulations which have recently been used as sun blocking agents. From TEM images, the formulation referred as Eusolex T-2000 included needle structures bearing a strong resemblance to those observed in this study. If so, then it is possible this is one of the first examples in which manufactured nanoparticles have been detected in the atmospheric environment.

Organic carbon and the inorganic salts $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 were not observed as separate entities. Nitrogen gives a very weak EDX signal (somewhat easily subsumed or confused with carbon and oxygen) and NH_4NO_3 is a volatile substance and would be beam sensitive. Organic carbon is likely to be adsorbed to elemental carbon and occur as a film on the surface of soot spherules (Chen et al., 2006; Wittmaack, 2005) or vaporise and appear as a contaminant film on the support grid. It is believed that particles (many of which were found to be beam sensitive) containing S, Na, Cl, Mg, K, O and C and tending to be non-aggregates and a mixture of amorphous and crystalline forms, actually included complex sulphate salts.

4.2. Intercomparison of TEM and ATOFMS data

The period of sampling was only two hours, but nonetheless, 600 particles have been examined by TEM and the ATOFMS measured about 1300 particles during this period and these have been classified according to the major clusters identified from the sampling of about 135,000 particles throughout the entire campaign. Nonetheless, the particle numbers are overall relatively

modest and consequently quantitative comparisons of abundance do not appear warranted. Also, we have not attempted to interpret vertical gradients shown in the TEM data, again because of doubts over statistical significance.

Table 1 lists the main TEM particle types and it attempts to assign sources and to highlight the most likely matching ATOFMS particles types where they exist. Although some approximate matches are achieved, there is overall a very low overlap between particles identified by the two techniques. Of the 8 TEM particle types listed, tentative matches are available for only 3 particle types. The others do not have direct equivalents in the ATOFMS data. Looked at from the other aspect, 15 ATOFMS particle types were identified during the campaign and 13 were identified during the period of sampling on 13 October 2006, however of these 13, only 5 (Ca-EC, OC, EC, Fe, NaCl and aged NaCl) have approximate matches in the TEM data.

The two amorphous carbonaceous aggregate types (without and with iron) are typical of carbonaceous clusters derived from combustion sources of which diesel vehicles are the predominant source in the urban atmosphere. Frequently, trace metals are associated with these particles as a result of their presence in fuel additives, engine oil and possibly atmospheric coagulation processes. Such particles are identified by the ATOFMS as the types Ca-EC, OC, and EC. The Ca-EC particle type was the most abundant of these within the campaign and has been observed previously in both field and laboratory studies as an emission product of diesel engines, combining carbon from incomplete combustion with calcium from oil additives. The EC particle type is similar but lacking the calcium, and the OC particle type, although showing many signals due to organic compounds, also shows minor spectral peaks due to elemental carbon. Consequently, particles from the diesel engine source appear to be identified relatively well by both techniques.

The iron-rich ATOFMS particle type shows internal mixing with sodium, nitrate, sulphate and elemental carbon and during this campaign was associated particularly with long-range transport processes. It therefore seems likely to have come from a high temperature source and to have been substantially processed during atmospheric transport. The TEM shows a major iron enrichment in both the iron-rich crystalline aggregate and the iron-rich crystalline non-aggregate particle type. These both show signals associated with other crustal elements such as Ti and Ca and it seems likely that these have a crustal origin, probably from soil or road dust. Particles of this nature have previously been identified in ATOFMS studies (e.g. Dall'Osto and Harrison, 2006) but none were identified during this campaign.

The TEM particle type with prominent peaks due to Na and Cl but also containing C, O, Mg, S, K and Ca seemed likely to be sea salt

Table 1
Comparison of main TEM particle types with ATOFMS particle types.

TEM particle type	ATOFMS particle equivalent	Likely origin
Amorphous carbonaceous aggregate	Ca-EC; OC; EC	Diesel exhaust
Amorphous carbonaceous aggregate containing iron	Fe	Diesel exhaust
Crystalline, non-aggregate, prominent Na, Cl	NaCl, aged NaCl	Sea salt with other water-soluble components
Fe-rich, crystalline aggregate	Not seen	Soil
Fe-rich, non-crystalline aggregate	Not seen	Soil; road dust
Ca-rich aggregate	Not seen	Soil; road dust
Sn-rich crystalline aggregate	Not seen	Brake dust (?)
Ti-rich, crystalline non-aggregate	Not seen	Paint?

derived with subsequent ageing. The ATOFMS is very effective at identifying both pure and aged sodium chloride particles and these are tentatively concluded to be equivalent to the TEM particle type.

It would be expected that several of the ATOFMS particle types would not be identified by the TEM. These include LRT nitrate, local nitrate, amine, HMOC (high mass organic carbon), MSA and SOA-PAH, all of which are expected to be semi-volatile and therefore liable to vaporise in the high vacuum environment of the TEM and therefore not be observed. Alternatively some of these species may easily polymerise under the electron beam and be evident as amorphous contamination products on the surface of the carbon support film. Therefore, arguably, all of those ATOFMS particle types expected to be involatile in the TEM were clearly observed in the TEM study. However, the TEM also identifies a range of metal-rich particle types, which were not observed by the ATOFMS. These include most notably the Sn-rich particle and the Ti-rich particles. Atmospheric concentrations of Sn and Ti are expected to be very low in the UK urban atmosphere and this fact, combined with a possibly low ATOFMS sensitivity to these elements (the ATOFMS shows an extremely high level of differential sensitivity to different elements), may explain the lack of detection of these particle types amongst the major clusters observed.

5. Conclusions

We have previously argued that the ATOFMS and the Aerodyne aerosol mass spectrometer (AMS) are complementary instruments whose combination is very powerful in elucidating atmospheric chemical processes. This complementarity arises primarily from the fact that both instruments give a very incomplete picture of the atmospheric aerosol but in combination they give a much fuller picture than either instrument individually. The ATOFMS can in theory identify all components of an airborne particle but in practice it is a highly imperfect instrument with strong matrix effects and differential sensitivities to different elements and it has a tendency to give a very biased view of aerosol composition. On the other hand, the AMS is limited to a rather small number of non-refractory components but has the advantage of giving continuous concentration data for those constituents, but as an aggregate rather than from single particles. The Transmission Electronic Microscope arguably also offers a complementary technique. It has the advantages of measuring across a wider range of sizes, from nanometres through micrometres, than either the ATOFMS or AMS and of establishing particle morphology as well as major element composition. As this study has shown, its major weakness is in loss of the semi-volatile components, which means that important constituents such as nitrate are lost prior to analysis and the rich information derived by both the AMS and ATOFMS from the mass spectra of organic components of the aerosol is entirely unavailable through the TEM. Consequently, even more than the ATOFMS, the TEM gives a very biased picture of aerosol composition. Its most suited application would appear to be in the source tracing of involatile particle components and especially those rich in metals. However, unlike the ATOFMS, which is capable of measuring the size and mass spectra of thousands of particles per hour allowing time series of individual particle types to be established, the TEM analysis is manual and highly laborious and consequently only very limited numbers of particles can be analysed with the associated low statistical significance of the outcomes. Both the ATOFMS and TEM provide valuable information on the internal mixing of particles but this has the disadvantage that subtle changes in overall particle composition are frequently observed due to differing levels of internal mixing and this leads to difficulties in classifying particles into a manageable number of groups.

Appendix A. Supplementary data

Supplementary data related to this article can be found at doi: [10.1016/j.atmosenv.2012.08.028](https://doi.org/10.1016/j.atmosenv.2012.08.028).

References

- Adachi, K., Tainosho, Y., 2004. Characterization of heavy metal particles embedded in tire dust. *Environment International* 30, 1009–1017.
- Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M., Armstrong, B., 2010. Urban ambient particle metrics and health: a time series analysis. *Epidemiology* 21, 501–511.
- Barlow, J.F., Dunbar, T.M., Nemitz, E.G., Wood, C.R., Gallagher, M.W., Davies, F., O'Connor, E., Harrison, R.M., 2011. Boundary layer dynamics over London, UK, as observed using doppler Lidar during REPARTEE-II. *Atmospheric Chemistry and Physics* 11, 2111–2125.
- Bérubé, K.A., Jones, T.P., Williamson, B.J., Winters, C., Morgan, A.J., Richards, R.J., 1999. Physicochemical characterisation of diesel exhaust particles: factors for assessing biological activity. *Atmospheric Environment* 33, 1599–1614.
- Calvert, C., Brown, A., Brydson, R., Lingard, J., Tomlin, A., Smith, S., 2003. Characterisation of the <500 nm fraction of airborne particulates using TEM, EDX and EELS. *Institute of Physics Conference Series* 179, 323–326.
- Calvert, C.C., Brown, A.P., Brydson, R., 2005. Determination of the local chemistry of iron in inorganic and organic materials. *Journal of Electron Spectroscopy and Related Phenomena* 143, 173–187.
- Chen, Y., Shah, N., Huggins, F.E., Huffman, G.P., 2006. Microanalysis of ambient particles from Lexington, KY, by electron microscopy. *Atmospheric Environment* 40, 651–663.
- Colbeck, I., Appleby, L., Hardman, E.J., Harrison, R.M., 1990. The optical properties and morphology of cloud-processed carbonaceous smoke. *Journal of Aerosol Science* 21, 527–538.
- Dall'Osto, M., Harrison, R.M., Coe, H., Williams, P.I., Allan, J.D., 2009a. Real time chemical characterization of local and regional nitrate aerosols. *Atmospheric Chemistry and Physics* 9, 3709–3720.
- Dall'Osto, M., Harrison, R.M., Coe, H., Williams, P., 2009b. Real-time secondary aerosol formation during a fog event in London. *Atmospheric Chemistry and Physics* 9, 2459–2469.
- Dall'Osto, M., Harrison, R.M., 2006. Chemical characterisation of single airborne particles in Athens (Greece) by ATOFMS. *Atmospheric Environment* 40, 7614–7631.
- Dall'Osto, M., Harrison, R.M., 2012. Urban organic aerosols measured by single particle mass spectrometry in the megacity of London. *Atmospheric Chemistry and Physics* 12, 4127–4142.
- Dockery, D.W., Pope, C.A., Xu, X., 1993. An association between air pollution and mortality in six US cities. *New England Journal of Medicine* 329, 1753–1759.
- Duffin, R., Clouter, A., Brown, D., Tran, C.L., MacNee, W., Stone, V., Donaldson, K., 2002. The importance of surface area and specific reactivity in the acute pulmonary inflammatory response to particles. *Annals of Occupational Hygiene* 46, 242–245.
- Esquivel, E.V., Murr, L.E., 2004. A TEM analysis of nanoparticles in a Polar ice core. *Materials Characterization* 52, 15–25.
- Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M., 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmospheric Environment* 44, 141–146.
- Gross, D.S., Galli, M.E., Silva, P.J., Wood, S.H., Liu, D.-Y., Prather, K.A., 2000. Single particle characterization of automobile and diesel truck emissions in the Caldecott Tunnel. *Aerosol Science and Technology* 32, 152–163.
- Gualtieri, M., Andrioletti, M., Mantecca, P., Vismara, C., Camatini, M., 2005. Impact of tire debris on in vitro and in vivo systems. *Particle and Fibre Toxicology* 2 (1). <http://dx.doi.org/10.1186/1743-8977-2-1>.
- Harrison, R.M., Dall'Osto, M., Beddows, D.C.S., Thorpe, A.J., Bloss, W.J., Allan, J.D., Coe, H., Dorsey, J.R., Gallagher, M., Martin, C., Whitehead, J., Williams, P.I., Jones, R.L., Langridge, J.M., Benton, A.K., Ball, S.M., Langford, B., Hewitt, C.N., Davison, B., Martin, D., Petersson, K., Henshaw, S.J., White, I.R., Shallcross, D.E., Barlow, J.F., Dunbar, T., Davies, F., Nemitz, E.G., Phillips, G.J., Helfter, C., Di Marco, C.F., Smith, S., 2012. Atmospheric chemistry and physics in the atmosphere of a developed megacity (London): an overview of the REPARTEE experiment and its conclusions. *Atmospheric Chemistry Physics* 12, 1–50.
- Harrison, R.M., Jones, A.M., Lawrence, R.G., 2003. Pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. *Atmospheric Environment* 37, 4927–4933.
- Health Effects Institute, 2000. Re-analysis of the Harvard Six-cities Study and the American Cancer Society Study of Particulate Air Pollution and Mortality. A Special Report of the Institute's Particles Epidemiology Reanalysis Project, Health Effects Institute, Cambridge MA.
- Johnson, K.S., Zuberi, B., Molina, L.T., Molina, M.J., Iedema, M.J., Cowin, J.P., Gaspar, D.J., Wang, C., Laskin, A., 2005. Processing of soot in an urban environment: case study from the Mexico City metropolitan area. *Atmospheric Chemistry and Physics* 5, 3033–3043.
- Kapp, N., Kreyling, W., Schulz, H., Hof, V.I., Gehr, P., Semmler, M., Geiser, M., 2004. Electron energy loss spectroscopy for analysis of inhaled ultrafine particles in rat lungs. *Microscopy Research and Technique* 63, 298–305.

- Kirchner, U., Scheer, V., Vogt, R., Kägi, R., 2009. TEM study on volatility and potential presence of solid cores in nucleation mode particles from diesel powered passenger cars. *Journal of Aerosol Science* 40, 55–64.
- Kocbach, A., Johanse, B.V., Scharze, P.E., Namork, E., 2005. Analytical electron microscopy of combustion particles: a comparison of vehicle exhaust and residential wood smoke. *Science of the Total Environment* 346, 231–243.
- Laden, F., Neas, L.M., Dockery, D.W., Schwartz, J., 2000. Association of fine particulate matter from different sources with daily mortality in six US cities. *Environment Health Perspectives* 108 (10), 941–947.
- Lin Yi-Hung, 2005. Microanalytical Characterization of Airborne Particulate Matter. MSc thesis, University of Leeds, UK.
- Murr, L.E., Bang, J.J., 2003. Electron microscope comparisons of fine and ultra-fine carbonaceous airborne particulates. *Atmospheric Environment* 37, 4795–4806.
- Murr, L.E., Garza, K.M., 2009. Natural and anthropogenic nanoparticles: their microstructural characterization and respiratory health implications. *Atmospheric Environment* 43, 2683–2692.
- Peng, R.D., Bell, M.L., Geyh, A.S., McDermott, A., Zeger, S.L., Samet, J.M., Dominici, F., 2009. Emergency admissions for cardiovascular and respiratory diseases and the chemical composition of fine particle air pollution. *Environmental Health Perspectives* 117, 957–963.
- Pope, C.A., Burnett, R.J., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association* 287, 1132–1141.
- Pope, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J., 2004. Cardiovascular mortality and long-term exposure to particulate air pollution. *Circulation* 109, 71–77.
- Pósfai, M., Anderson, J.R., Buseck, P.R., Shattuck, T.W., Tindale, N.W., 1994. Constituents of a remote Pacific marine aerosol: a TEM study. *Atmospheric Environment* 28, 1747–1756.
- Schulz, J., Hohenberg, H., Pflücker, F., Gärtner, E., Will, T., Pfeiffer, S., Wepf, R., Wendel, V., Gers-Barlag, H., Wittern, K.-P., 2002. Distribution of sunscreens on skin. *Advanced Drug Delivery Reviews* 54 (Suppl. 1), S157–S163.
- Silva, P.J., Prather, K.A., 2000. Interpretation of mass spectra from organic compounds in aerosol time-of-flight mass spectrometry. *Analytical Chemistry* 72, 3553–3562.
- Song, X.H., Hopke, P.K., Fergenson, D.P., Prather, K.A., 1999. Classification of single particles analyzed by ATOFMS using an artificial neural network, ART-2A. *Analytical Chemistry* 71, 860–865.
- Wentzel, M., Gorzawski, H., Naumann, K.-H., Saathoff, H., Weinbruch, S., 2003. Transmission electron microscopical and aerosol dynamical characterization of soot aerosols. *Journal of Aerosol Science* 34, 1347–1370.
- WHO, 2004. Meta-analysis of Time-series Studies and Panel Studies of Particulate Matter (PM) and Ozone (O₃). WHO Regional Office for Europe, Copenhagen.
- Williams, D.B., Carter, C.B., 1996. *Transmission Electron Microscopy: a Textbook for Materials Science*. Plenum, NY.
- Wittmaack, K., 2005. Combustion characteristics of water-insoluble elemental and organic carbon in size selected ambient aerosol particles. *Atmospheric Chemistry and Physics* 5, 1905–1913.