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Seasonal variation of fine particulate composition in the centre of a UK city

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ABSTRACT

In order to better project the impacts of air quality control measures, it is necessary to study the behaviour of particulates beyond mass-based metrics. To study the long term and seasonal trends of particulate chemical composition in Manchester, UK, seven Aerosol Mass Spectrometer (AMS) datasets obtained from ambient sampling in central Manchester over a seven year period have been combined and compared. The size-resolved submicron nitrate, sulphate, ammonium and organic matter data were examined to assess the relative importance of season, local meteorology and synoptic transport in determining ambient concentrations. Systematic trends were observed that were not previously possible through the analysis of individual datasets in isolation.

The results obtained here indicate that prevailing westerly winds tend to bring relatively consistent low levels of pollutants, whereas Easterly and Northerly winds bring much more variable pollutant concentrations, whose chemical compositions are strongly dependent on season. Specifically, continental air in the summer brings with it high levels of sulphates whereas in winter similar synoptic conditions and cold ground temperatures tend to induce strong inversions, trapping local pollution and leading to elevated organic matter. Local temperature was also found to be important, with the very low temperatures in winter and very high temperatures in summer giving the greatest concentrations of all components except ammonium nitrate in summer, which began to evaporate at the higher temperatures. These results will assist in evaluating the chemical nature of air pollution episodes and also provide a phenomenological basis for testing chemical transport and exposure models. While the results focus on Manchester, similar phenomena could be expected of a number of UK cities.

1. Introduction

Fine particulates remain an important topic in air quality, as they are known to affect human health and visibility (Brunekreef and Holgate, 2002; Hyslop, 2009). Not only have high concentrations of particulates been linked numerous times to detrimental health effects – including asthma and cardiovascular disease (Dockery et al., 1993; Pope et al., 2002) but certain specific pollutants may cause more harmful effects than others (Mauderly and Chow, 2008; Nemmar et al., 2001). In addition, particulates, including urban particulates, are known to have a significant effect on climate through scattering solar radiation and perturbing cloud properties (Choularton et al., 2008; Forster et al., 2007), however the exact magnitude of their effects is currently very uncertain and represents a major challenge in climate science (Textor et al., 2006). Because particulates have a much shorter lifetime in the atmosphere compared to gases such as carbon dioxide and methane, their effects can be particularly pronounced on regional scales, perturbing clouds and precipitation in particular (Lohmann and Feichter, 2005; Ramanathan and Carmichael, 2008; Shindell and Faluvegi, 2009).

Limiting particulate exposure is recognised as a key priority for legislators and it is subject to regulation at a European level (European Union, 2008). However, in spite of measures taken over the years, concentrations have not decreased as projected (DEFRA, 2007). This necessitates improving our understanding of the factors controlling particulates in greater detail.

The main metric that has been employed during automated air quality monitoring activities in the UK over recent decades is the PM_{10}, using either beta attenuation gauges or Tapered Element Oscillating Micro-balances (TEOMs). More recently, the UK measurement has included $PM_{2.5}$. These are related to the reference method of gravimetric weighing of filter samples that forms the basis of air quality legislation (Bureau Veritas, 2006). The limitation of total mass measurements such as this is that they do not capture changes in composition, which are useful in both identification of sources and the provision of more detailed exposure assessments

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(Putaud et al., 2004). There are a number of different methods that are available for this purpose, although these tend to be much less widespread than the total mass measurements. The most common being the offline analysis of collected filter samples in the laboratory. This comes with a number of intrinsic limitations, such as the labour intensity associated with the collection and analysis of the samples, the long sampling times (typically 12–24 h) and the loss of semivolatiles (such as ammonium nitrate), although the Filter Dynamics Measurement System (FDMS) TEOM does address the latter issue. To address these limitations, a number of instruments have been developed by various manufacturers that perform the analysis in situ in either a continuous or semi continuous manner (Laj et al., 2009, and references therein). Examples include soluble ion analysis such as that used in the Applikon MARGA (ten Brink et al., 2007) and Particle Into Liquid Sampler (Weber et al., 2001) or evolved gas analysis, as used in the Sunset Labs EC/OC analyser (Bae et al., 2004). However, these techniques are still typically limited to a time resolution of hours and do not deliver any size-resolved information.

Another type of in situ instrument is the Aerodyne Aerosol Mass Spectrometer (AMS) (Canagaratna et al., 2007). This provides a highly time resolved and very precise measurement of the non-refractory components of fine particulates, delivering data on a time resolution of minutes or less. Because it uses thermal vaporisation at around 600 °C, it is limited to the measurement of the components that will vaporise at this temperature (operationally defined as the ‘non-refractory’ fraction). It is also limited to particles of sizes that will transmit through the aerodynamic lens. This is nominally 30–700 nm for most of the data presented here, although some particles of larger sizes will be transmitted (Zhang et al., 2002, 2004).

The AMS is also capable of delivering size-resolved data by using aerodynamic sizing. Unfortunately, due to its relatively high running costs and labour intensity, measurements are typically confined to short-term, intensive campaigns of around a month in duration. To date, only a very small number of long-term measurement campaigns have been performed with this instrument (e.g. Lun et al., 2009; Takegawa et al., 2006). In the future, the new, lower cost Aerodyne Aerosol Chemical Speciation Monitor (ACSM) will undoubtedly produce many more long-term datasets of an equivalent nature to the AMS (Ng et al., 2010).

Here we present several sets of intensive measurements that have taken place within central Manchester between 2001 and 2007, covering 105 days of measurements. These were either as part of larger measurement campaigns or to evaluate instrument performance. Previously, a significant difference between winter and summer was noted by Allan et al. (2003a), which was further highlighted by Zhang et al. (2007). It was found that the summer conditions gave considerably greater mass concentrations for the secondary species while the winter more strongly favoured primary emissions. However, this was the result of comparing only two specific measurement periods during 2001 and 2002.

The purpose of this work is to collate all previous AMS datasets collected in central Manchester and compare them systematically to evaluate seasonal trends in aerosol composition more thoroughly and to establish the controlling factors responsible for each chemical constituent. The data are systematically compared with synoptic transport and local meteorology, so as to assess the importance of both local and regional influences. These are placed in the context of the long-term air quality and meteorological data to assess the applicability of the limited data available to the time period covered as a whole. This assessment will be of value when interpreting air quality data in this or other comparable cities and also for the evaluation of chemical transport or air quality exposure models.

2. Methodology

2.1. Aerosol mass spectrometer

Two models of AMS were used in these campaigns, the original quadrupole (quad) based design (Jayne et al., 2000) and the newer, more sensitive compact time-of-flight (C-ToF) design (Drewnick et al., 2005), though they both perform similar tasks: measurements of the chemical breakdown of particles sized between approximately 30 and 700 nm with a time resolution of minutes. The use of the C-ToF instrument effectively leads to an improvement in sensitivity and signal-to-noise ratio (Allan et al., 2010; Drewnick et al., 2009). The data were processed according to the standard analysis methods (Allan et al., 2004b, 2003b). In all cases, a collection efficiency of 0.5 was used, consistent with Matthew et al. (2008). While no drying was employed on the inlet flow, the ambient dew point was consistently much less than the laboratory temperature, ensuring that the aerosol was effectively sampled dry and the collection efficiency would be unaffected (Allan et al., 2004a). This collection efficiency is consistent with other urban deployments where external validations were available (e.g. Allan et al., 2010).

For this study, the data analysis has focussed on only the mass size distributions of particulate nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and organic matter (OM). These chemical species represent the majority of submicron non-refractory particulates in polluted environments (Zhang et al., 2007). The instrument was also capable of detecting ammonium chloride, however this tended to form short, very episodic events in these datasets, so no significant statistics could be generated. As such, chloride has been excluded from this analysis. Further data can be obtained from the organic fraction using numerical factorisation (e.g. Lanz et al., 2007; Ulbrich et al., 2009; Zhang et al., 2005), however doing this across multiple datasets is a significant undertaking (c.f. Lanz et al., 2010) and considered outside the scope of this work. Analysis of marker peaks such as m/z 44, 57 and 60 was not performed, as this would not capture all of the variability already known to exist within these datasets. Specifically, the significant cooking factor identified by Allan et al. (2010) would be unconstrained. For analysis of individual projects, the reader is directed to Zhang et al. (2007), Allan et al. (2010) and Jimenez et al. (2009). Allan et al. (2010) in particular presents the diurnal signatures that are present at this site.

Data from the two different AMS models were used, encompassing work from 6 different field campaigns and at 3 different Manchester city centre sites, as outlined in Table 1. The names are assigned according to season (summer/winter/autumn) and year. Where there are multiple datasets per measurement period, an additional qualifier is added to distinguish the measurements (explained below). Some of the measurements (specifically Sum01, Win02 and Win07) were performed on an ad hoc basis for the purposes of instrument characterisation (Allan et al., 2003a, 2010), whereas others formed part of larger projects. Specifically, Aut03

Table 1
Details of each of the individual campaigns, including campaign name, dates of the campaign period, location and AMS model.

Campaign Name	Year	Dates	Loc	AMS model
Sum01	2001	14/06/01–25/06/01	SSB	Quad
Win02	2002	17/01/02–28/01/02	SSB	Quad
Aut03	2003	15/09/03–17/09/03	SSB	Quad
Sum05	2005	31/05/05–29/07/05	SSB	Quad
Sum06/DH	2006	18/05/06–25/05/06	DH	C-ToF
Sum06/PT	2006	06/05/06–08/06/06	PT	Quad
Win07	2007	23/01/07–07/02/07	SSB	Quad