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Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign☆

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ABSTRACT

London, like many major cities, has a noted air pollution problem, and a better understanding of the sources of airborne particles in the different size fractions will facilitate the implementation and effectiveness of control strategies to reduce air pollution. Thus, the trace elemental composition of the fine and coarse fraction were analysed at hourly time resolution at urban background (North Kensington, NK) and roadside (Marylebone Road, MR) sites within central London. Unlike previous work, the current study focuses on measurements during the summer providing a snapshot of contributing sources, utilising the high time resolution to improve source identification. Roadside enrichment was observed for a large number of elements associated with traffic emissions (Al, S, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb and Zr), while those elements that are typically from more regional sources (e.g. Na, Cl, S and K) were not found to have an appreciable increment. Positive Matrix Factorization (PMF) was applied for the source apportionment of the particle mass at both sites with similar sources being identified, including sea salt, airborne soil, traffic emissions, secondary inorganic aerosols and a Zn-Pb source. In the fine fraction, traffic emissions was the largest contributing source at MR (31.9%), whereas it was incorporated within an "urban background" source at NK, which had contributions from wood smoke, vehicle emissions and secondary particles. Regional sources were the major contributors to the coarse fraction at both sites. Secondary inorganic aerosols (which contained influences from shipping emissions and coal combustion) source factors accounted for around 33% of the PM_{10} at NK and were found to have the highest contributions from regional sources, including from the European mainland. Exhaust and non-exhaust sources both contribute appreciably to PM_{10} levels at the MR site, highlighting the continuing importance of vehicle-related air pollutants at roadside.

1. Introduction

Exposure to airborne particles, both short and long-term, has been linked with a number of detrimental effects on human health (Cohen et al., 2005; Kampa and Castanas, 2008). The size and chemical composition of airborne particles are thought to be key factors affecting their toxicity (Heal et al., 2012). Smaller particles are thought by many to be more harmful than larger particles, and clear relationships have been observed between exposure to fine particles ($PM_{2.5}$, particles with an aerodynamic diameter less than 2.5 μm) and adverse health effects (Brook et al., 2010; Pope et al., 2002). As a result, $PM_{2.5}$ is an air pollution metric widely used to assess air quality, with the EU having set targets for reduction in $PM_{2.5}$ levels and population exposure.

In an urban environment, there are a number of sources, both natural and anthropogenic, which emit particles across a broad size

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range. Sources typically differ for fine and coarse fractions, with fine particles most often from anthropogenic combustion sources, such as vehicle tailpipes, industrial emissions and biomass burning, and from secondary production within the atmosphere. In contrast, particles in the coarse fraction ($PM_{2.5-10,}$ particles with an aerodynamic diameter between 2.5 and 10 μm) mainly arise from abrasion processes and can include crustal material and vehicle wear products (Minguillón et al., 2012; Richard et al., 2011). While trace metals typically only constitute a small proportion of the total particle mass (as low as 1% (Handler et al., 2008)), analysis of the elemental composition of ambient fine and coarse particle fractions can be effective in determining source contributions, particularly for measurements performed at a high time resolution (Gao et al., 2016; Visser et al., 2015a; Dall'Osto et al., 2013; Moreno et al., 2011; Viana et al., 2008).

London, like many major cities, has a noted air pollution problem, and a better understanding of the sources of airborne particles in the different size fractions will facilitate the implementation and effectiveness of control strategies to reduce air pollution. As a result there has been a concerted recent effort to characterise the sources of airborne particles in London, notably as part of the REgents PARk and Tower Environmental Experiment (REPARTEE) and Clean Air for London (ClearfLo) projects (Harrison et al., 2012a; Bohnenstengel et al., 2015). The ClearfLo project, included both long-term studies (e.g. Young et al., 2015a) as well as summer and winter intensive observational periods. There have been a number of source apportionment studies that have focused on the winter measurements investigating organic aerosols (Yin et al., 2015; Young et al., 2015b) and trace elemental datasets (Visser et al., 2015a). From these source apportionment studies it was found that during winter, major sources of primary organic aerosols were vehicle emissions and cooking (Yin et al., 2015). In addition, coarse fraction particles ($PM_{2.5-10}$) were influenced primarily by marine factors and traffic emissions whereas particles in the fine fraction (PM_1) were predominantly from more regional sources in winter (S-rich and solid fuel burning, Visser et al., 2015a).

A previous source apportionment analysis of a long-term (2 year) dataset comprising mainly trace element concentrations at an urban background site in London determined six sources; Urban background, Marine, Secondary, Non-exhaust traffic/Crustal, Fuel oil and Traffic (Beddows et al., 2015). This analysis was unable to fully resolve the traffic contributions, with the urban background source factor found to have a strong traffic signature, possibly due to the low time resolution (daily) of the measured elemental concentrations. Therefore in the present work we analyse trace elemental composition of particles in the fine and coarse fractions at an urban background and roadside site in London collected at a high (hourly) temporal resolution, with the aim to improve the source apportionment, particularly of traffic emissions. In contrast to previous studies in London using elemental analysis (Beddows et al., 2015; Visser et al., 2015a, 2015b), the current work focusses on measurements during the summer, and thus provides a snapshot of the contributing sources for this period. The results are compared at both roadside and urban background sites, in order to examine the contribution of vehicle emissions and its source characteristics. We employ a receptor model, Positive Matrix Factorization (PMF), to apportion the sources at both sites, utilising the high time resolution of the elemental data to improve the source identification. The resultant sources and size fractions determined for each site are compared to examine the differences in contributing sources.

2. Method

2.1. Sampling sites

The measurements were a part of the ClearfLo project (Clean Air for London, www.clearflo.ac.uk), which aimed to investigate boundary layer pollution in London; an overview is provided by Bohnenstengel et al. (2015). Sampling was conducted during the summer intensive observation period in July–August 2012 at two sites located within central London. The first site, classified as urban background, was within a school grounds in a residential area of North Kensington (NK). The air pollution climate at NK has been described in detail by Bigi and Harrison (2010), and is considered as representative of the background air quality for most of London. The second site, classified as roadside, was located 1 m from Marylebone Road (MR), a busy six lane road (ca. 80,000 vehicles a day) in central London. Both sites are also permanent stations of the Automatic Urban and Rural Network (AURN) from which monitoring data for the classical air pollutants were obtained. At both sampling sites black carbon (BC, 2 wavelength Aethalometer), nitrate (URG-9000B ambient ion monitor), NO_x (chemiluminescence) and $PM_{2.5}$ mass concentrations (FDMS-TEOM) were obtained from the national AURN and Speciation Networks. PM_{10} mass concentrations were available from the AURN for NK but not at MR due to instrument malfunction. A map detailing the locations of the sampling sites can be found in Bohnenstengel et al. (2015).

2.2. Sampling methodology and instrumentation

Aerosol samples were collected by low volume continuous 'Streaker' samplers, which allowed the determination of the elemental concentrations with hourly resolution, in both the fine ($D_a < 2.5$ μm) and the coarse (2.5 μm $< D_a <$ 10 μm) fraction of particulate matter (Crespo et al., 2012; D'Alessandro et al., 2003). Briefly, in a Streaker sampler, particles are separated in two different stages by a pre-impactor and an impactor. The pre-impactor removes particulate matter with aerodynamic diameter $D_{ae} > 10$ μm. The aerosol coarse fraction impacts on a Kapton foil where it is deposited while the fine fraction is collected on a Nuclepore filter having 0.4 μm pores. The two collecting plates (Kapton and Nuclepore) are paired on a cartridge, which rotates at constant speed (~1.8° per hour) for a week: this produces a circular continuous deposit of particular matter (the 'streak') on both stages.

The resulting samples were analysed via PIXE (Particle-Induced X-Ray Emission) performed with 2.7 MeV protons from the 3 MV Tandetron accelerator of the **L**aboratorio di tecniche nucleari per l'**A**mbiente e i **BE**ni **C**ulturali (LABEC) laboratory of Istituto Nazionale di Fisica Nucleare (INFN) in Florence, with the external beam set-up described extensively elsewhere (Lucarelli et al., 2014). The beam (30–200 nA) scanned the streak in steps corresponding to 1 h of aerosol sampling; each spot was irradiated for about 180 s. The resulting PIXE spectra were fitted using the GUPIX software package (Maxwell et al., 1995) and elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density. The uncertainty of hourly elemental concentrations was determined by a combination of independent uncertainties in: standard sample thickness (5%), sampling parameters (5%) and X-ray counting statistics (2–20%). Detection limits were about 10 ng m^{-3} for low-atomic number elements and 1 ng m^{-3} or below for medium-high atomic number elements. The following elements were detected: Na, Mg, Al, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Pb. Occasionally Bi was also detected. Unfortunately, the Nuclepore filters were contaminated by Si and Br whose ambient concentrations were consequently not possible to determine. We