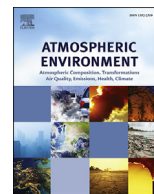




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# Atmospheric Environment

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## Characterisation of iron-rich atmospheric submicrometre particles in the roadside environment



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### HIGHLIGHTS

- Airborne particles sampled with nano-MOUDI impactor.
- Many particles with high and moderate Fe content.
- Clusters comprised of primary particles of 20–30 nm diameter.
- Iron oxides are identified by TEM-EELS and are externally mixed.

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### ABSTRACT

Human exposure to ambient metallic nanoparticles is an area of great interest owing to their potential health impacts. Ambient metallic nanoparticles found in the roadside environment are contributed by combustion engines and wear of brakes, tyres and road surfaces. Submicrometre atmospheric particles collected at two UK urban sites have been subject to detailed characterisation. It is found that many metallic nanoparticles collected from roadside sampling sites are rich in iron. The Fe-rich nanoparticles can be classified into (1) high Fe content (ca 90 wt%) with each alloying element less than 1 wt%; and (2) moderate Fe content (<75 wt%) with high manganese and silicon content. Both clusters contain a variable mix of minor constituents, Mn, S and Si being most important in the high-Fe group. The moderate Fe group also contains Zn, Cu, Ba, Al and Ca. The Fe-rich nanoparticles exhibit primary particle sizes ranging between 20 and 30 nm, although some much larger particles up to around 100 nm can also be observed, along with some very small particles of 10 nm or less. These tend to agglomerate forming clusters ranging from ~200 nm to 1 µm in diameter. The iron-rich particles observed are oxides, taking the form of spheres or multifaceted regular polyhedra. Analysis by EELS shows that both high- and moderate-Fe groups include particles of FeO, Fe<sub>3</sub>O<sub>4</sub>, α-Fe<sub>2</sub>O<sub>3</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> of which γ-Fe<sub>2</sub>O<sub>3</sub> is the most prominent. Internal mixing of different Fe-oxides is not observed.

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### 1. Introduction

Iron is often present in substantial concentrations in airborne

particulate matter (e.g. Harrison et al., 2004). This is significant because iron rich particles exert an important role in some atmospheric chemical reactions, including the oxidation of S(IV) compounds such as SO<sub>2</sub> to S(VI) compounds such as H<sub>2</sub>SO<sub>4</sub> (Grgić et al., 1996), and on biogeochemical cycles – deposition of atmospheric iron influences marine productivity and therefore has a marked influence on the global carbon cycle (Mahowald et al., 2005).

Atmospheric iron is also known to have adverse effects on human health, being associated with inflammation and DNA damage via oxidative stress caused by generation of free radicals and

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reactive oxygen species (Gurzau et al., 2003). As the population are exposed to inhalable atmospheric iron from many sources, and given that iron is known to be biologically active and potentially harmful, its presence is a public health concern. Establishing the physical and chemical characteristics of the atmospheric iron burden, such as size distribution, particle morphology, chemical composition and oxidation state will therefore underpin assessments of the risks to human health from exposure.

Iron in atmospheric particulate matter originates from a number of crustal and anthropogenic sources (Sanderson et al., 2014). These include industrial and metallurgical processes (Buonanno et al., 2011; Cernuschi et al., 2012; Reinard et al., 2007), combustion of fossil fuels (Linak et al., 2007), emissions from transport sources such as diesel emissions (Liati et al., 2012; Patel et al., 2012), tyre wear (Adachi and Tainosho, 2004), brake wear (Kukutschová et al., 2011), shipping (Moldanová et al., 2009) and resuspension of crustal materials and road dust (Amato et al., 2011). Use of iron compounds as catalytic additives in automotive engines will also lead to emissions of iron. Although these reduce the total particulate emission from the engine, metallic oxides have been reported to be included in the soot emitted when such additives are used (Lee et al., 2006; Song et al., 2006).

Moreover, each of these sources contributes iron with differing physical and chemical properties resulting from the effect of their different formation processes. Previously reported examples include nanoparticulate  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> from fly ash (Linak et al., 2007), nanoparticulate Fe<sub>3</sub>O<sub>4</sub> from in-cylinder melting of engine wear fragments (Liati et al., 2015), various oxides, silicates and W and Cr alloys from waste-to-energy plants (Buonanno et al., 2011) and agglomerates of nanoparticles of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> from brake discs and pads (Kukutschová et al., 2011).

The project was established with a view to characterisation of metallic nanoparticles, with a particular interest in Fe because of its apparent biological activity (Zhou et al., 2003; Mahmoudi et al., 2012) and cerium which is used as a nano-particulate motor fuel additive, hence requiring evaluation of its environmental and human health consequences. Our results for cerium have been published elsewhere (Gantt et al., 2014, 2015). This paper aims to present comprehensive characterisation data for submicrometre atmospheric iron particles collected at two UK urban sites, including physical structure and morphology, and chemical composition, using analytical Transmission Electron Microscopy (TEM) techniques; namely Energy Dispersive Spectroscopy (EDS) and oxidation state data from Electron Energy Loss Spectroscopy (EELS). These are all important parameters influencing the interaction of these particles with biological systems.

## 2. Methodology

### 2.1. Details of sampling sites

Samples for electron microscope analysis were collected at two sampling sites in urban locations:

**Bristol Road Observatory:** This site is a traffic roadside site located at the South Entrance to the University of Birmingham campus, Edgbaston, adjacent to the A38 main road (approximately 4 m distance). Size segregated bulk filter samples and samples for TEM were collected here by nanoMOUDI. There is a large four-way intersection adjacent to the site controlled by traffic lights – consequently the traffic is frequently stopped directly adjacent to the sampling location. The most recent figures from the Department for Transport record an average annual daily flow (AADF) of 27,265 vehicles in 2011. HGVs account for 1.46% of this traffic and buses/coaches 2.4%. The site is slightly elevated relative to the road so the inlet was approximately 3–4 m above the road surface.

**Newcastle Civic Centre:** The Automatic Urban and Rural Network (AURN) station at Newcastle Civic Centre, Newcastle-upon-Tyne was used as a traffic roadside site to collect nanoMOUDI and MOUDI bulk filter and TEM grid samples. The site was chosen because Newcastle's public buses are run by a company which used cerium oxide fuel additives (Envirox) in their fleet in this area at the time of sampling. The physical and chemical composition of these samples would therefore make a useful comparison to the site in Birmingham, where cerium oxide additives are not used by the major local transport operators. No traffic flow data are available for the site.

### 2.2. Sample collection procedures

A nanoMOUDI-ii 125R cascade impactor (MSP Corporation) was used to collect size resolved particulate matter samples. The instrument has thirteen stages with nominal 50% cut-points of 10,000, 5600, 3200, 1800, 1000, 560, 320, 180, 100, 56, 32, 18 and 10 nm when operated at an inlet flow rate of 10.0 L/min. The impactor was paired with a Leybold SV 16 rotary vane oil pump in Newcastle, and a slightly more powerful SV 25 pump in Birmingham, although the difference in flow-rate between these pumps was negligible; the TEM samples were collected at ~9.5 L/min in both cases, which would make minimal difference to the stated cut-points.

The instrument separates particles into a series of logarithmically equal size fractions based on atmospheric diameter, by accelerating particles through a fine jet and impaction upon a filter substrate mounted below on a rotating plate which collects the heavier particles while the lighter ones follow in the gas streamline to the next stage. In practice the cut-off diameters can be affected by particle bounce and particle blow-off leading to larger than expected particles being detected in the lower stages. Some evidence of this has been seen in these samples.

The experimental set-up at the sampling sites had the impactor and pump housed in a cabinet, with an inlet at the top of the housing covered by a rain hood. Two fans were positioned next to the pump to keep it as cool as possible during operation, but nevertheless temperatures in the region of 40–45 °C during operation were still recorded, particularly during the summer months. This would have the effect of reducing the mass of semi-volatile material collected by this method in bulk samples, requiring long collection times.

TEM samples were collected by affixing conventional 3 mm copper support grids, with lacey or ultra-thin carbon films, to aluminium filter substrates, then sampling at the normal rate for the instrument. Sampling at Newcastle was carried out using one set of films over three sessions totalling 8 h which was found to give suitable particle number density on the smaller stages below 180 nm. The 2014 Birmingham samples were initially collected for three hours; this proved inadequate despite the higher concentrations at this site, so they were reloaded and sampled for an additional three hours. At both sites sample collection was carried out in the afternoon. The trade-off for getting useful particle numbers in the ultrafine/pseudo-ultrafine range was that particles in the fine and coarse range were somewhat too dense, with particles overlaying each other on the grid surface. However, the analysis of submicron particles was the priority of the project. In both cases samples were collected outside rush-hour in cold winter weather. The data presented in this paper derive from comprehensive evaluation of one nano-MOUDI sample per site, collected over three separate afternoons.

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