The Chemical Composition of Particulate Matter in Cork City Centre

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Introduction

Primary inorganic pollutant gases play an important role in atmospheric acidity. **Sulfur dioxide** is a primary inorganic pollutant that undergoes gas to particle conversion (heterogeneous reactions) and can take part in gas-phase (homogeneous) reactions to form secondary inorganic pollutants. These secondary pollutants formed in the atmosphere include acidic sulfate aerosols. **Ammonia** can exist in the atmosphere in relatively high concentrations in agriculturally intense regions and also in urban areas. It is one of the products of decaying plants and animals and is also associated with human activities such as fossil fuel burning, and vehicle emissions (Liu *et al.*, 1995). Acidic aerosols including bisulfate and sulfate aerosols can react with gaseous ammonia to form ammonium salts (Spengler *et al*,, 1990). Hence aerosol acidities are known to be lower in atmospheric regions where ready neutralisation of sulfates by reaction with ammonia occurs (Brook et al., 1997). Epidemiologic studies strongly suggest that human mortality and morbidity rates are associated with the presence of acid aerosols in ambient air (Spengler *et al*., 1990). Indeed Gwynn *et al*., (2000) found an association between both hydrogen ion and sulfate-containing particles and respiratory hospital admissions and mortality in Buffalo, U.S.A.

Experimental

Weekly samples of $PM_{2.5-0.1}$ and $PM_{10-2.5}$ were collected using a high volume cascade impactor running at 900 l min^{-1} (Fig 1) using pre-weighed polyurethane foam (PUF). Post collection, the samples were conditioned for one week in a dessicator and the samples re-weighed to obtain the dry particulate weight. Sections of the PUF were aqueous extracted and the extract filtered (0.22 µm pore size). The filtered samples were analysed for ammonium and sulfate ions using a Dionex ICS2000 ion chromatography system. **"Strong acidity"** was determined by following the method outlined by Pathak *et al* (2004) and, in accordance with this method, the **"free acidity"** and **"pH"** was determined using the online Atmospheric Inorganics Model 2 (AIM2) (Clegg *et al*., 1998, http://www.hpc1.uea.ac.uk/~e770/aim.html).

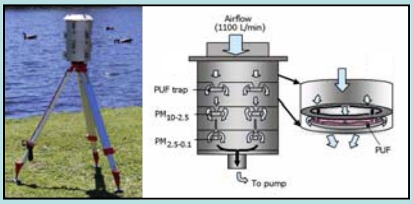

Fig 1. The three stage high volume cascade impactor, collecting $PM_{10-2.5}$ and $PM_{2.5-0.1}$ onto polyurethane foam.

Results

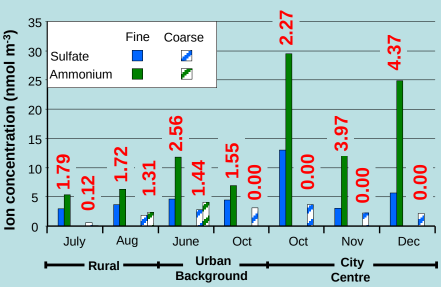

Fig 2. Inorganic particulate composition and ammonium to sulfate ratio (red).

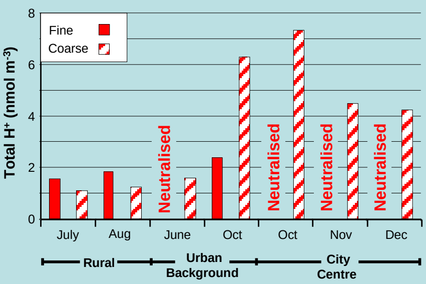

Fig 3. Strong acidity in terms of total nmol H^+ per m^3 of air.

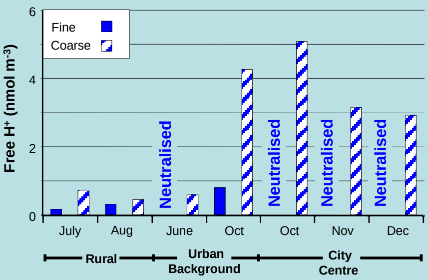

Fig 4. Free acidity in terms of free nmol H^+ per m^3 of air derived from the AIM2 model.

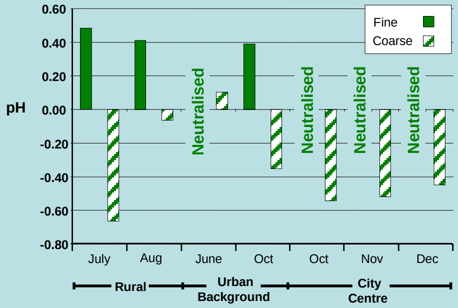

Fig 5. pH of fine and coarse aerosol derived from the AIM2 model.

The concentration of ammonium and sulfate ions was found to be highest at the City Centre site and lowest in the rural samples: the fine fraction was more enriched (Fig 2). Due to the high levels of ammonium ions in the fine fraction, the samples were either ammonium rich ($2>[NH_4^{+}]/[SO_4^{2-}]>1.5$) or completely neutralised ($[NH_4^{+}]/[SO_4^{2-}]>2$). All samples from the coarse fraction were deemed ammonium poor ($[NH_4^{+}]/[SO_4^{2-}]<1.5$).

	Rural	Urban Background	City Centre
Strong Acidity (Fig 3)	Greater in fine fraction compared to coarse	Lower or completely neutralised in fine fraction compared to coarse	Completely neutralised in fine fraction but present in coarse
Free Acidity (Fig 4)	Lower in fine fraction compared to coarse	Lower or completely neutralised in fine fraction compared to coarse	Completely neutralised in fine fraction but present in coarse
pH (Fig 5)	Positive pH in fine fraction and negative pH in coarse	Neutralised or positive pH in fine fraction and positive or negative pH in coarse	Fine fraction neutralised and negative pH in coarse

Conclusions

The Hong Kong reference study (Pathak *et al*., 2004) found the fine fraction to contribute significant acidity and showed higher concentrations of sulfate ions. In our study it was the fine fraction that was more enriched in ammonium and sulfate ions but has a lower acidity due to the high ammonium to sulfate ratio. The pH in the Cork samples was found to be higher than the reference study but this calculation assumes that the water content of aerosol had a density of 1. Future work will attempt to determine how the levels of ammonium and sulfate affect the density of water associated with the aerosol.

References

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