Linking urban field measurements of inhalable particulate matter to their chemical analysis and effects on health

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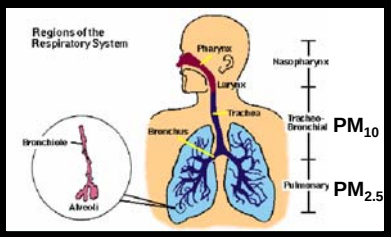
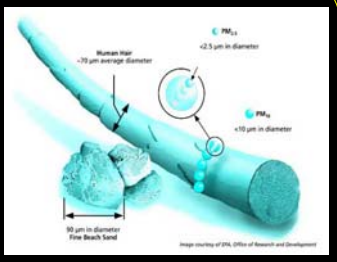
Introduction



Recent epidemiological studies have shown that atmospheric pollution caused by airborne particulate matter (PM) has a negative impact on human health. Chemical analysis shows PM to comprise of many inorganic (Trace metal/Inorganic ions), organic, and elemental materials, several of which are toxic. For example, solubilized metal ions such as zinc have been found to be linked to lung injury and polyaromatic hydrocarbons (PAHs) exhibit carcinogenic and or mutagenic properties, which cause marked stress on lung tissue. The metals can be found within the matrix of an insoluble component, within a soluble salt, and complexed at a surface. Metals which can be available in more than one stable valence state can catalyse an electron transfer and therefore demonstrate some capacity to generate oxidants. Therefore it is important to determine the contribution of metals and other chemical components, to the adverse health effects observed in PM epidemiology studies. The current study is the first of its kind in Ireland to quantitatively analyse, the chemical composition of ambient inhalable airborne particulate matter. It was motivated by the need to determine the concentrations of individual components within ambient PM over Cork City for different collected size fractions, as a prelude to the development of an appropriate source apportionment model and to cellular toxicity studies.



2003 - 2004 SAMPLING CAMPAIGN

Sampling Location

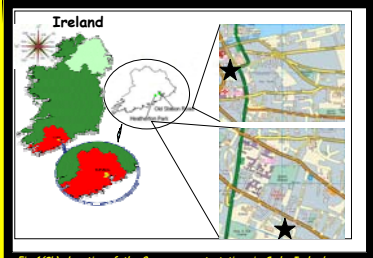


Fig 1(SL). Location of the 2 measurement stations in Cork, Ireland selected for the study.

Sampling equipment

Samples were collected using a dichotomous Partisol sampler (Fig 2(S)) monitoring for coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) fractions.

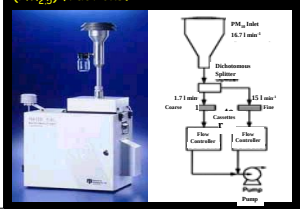


Fig 2(S). The Partisol sampler with the dichotomous splitter for the collection of PM10-2.5 and PM2.5 on PTFE filters.

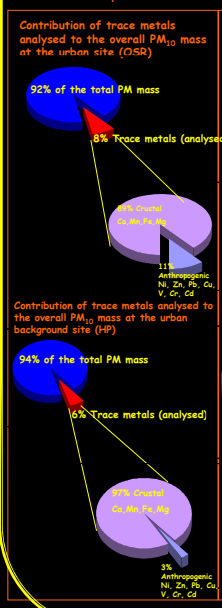
- Flow rate of 16.7 l min^{-1}
- PTFE (47 mm) collection filters
- Filters are flat providing an excellent substrate for electron microscopy, reflectometry and x-ray fluorescence.

RESULTS & DISCUSSION

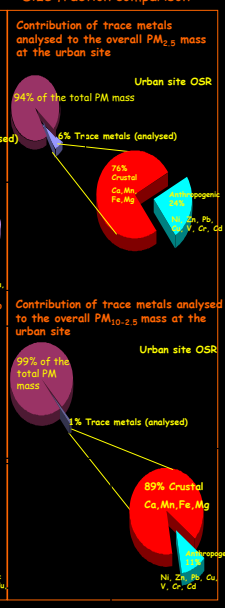
Trace metals

An acid/microwave digestion using HNO_3, HF and H_2O was performed on the filters to be analysed for trace metals. The liquid digested sample solutions were analysed using ICP-OES analysis. *(Ca, Mn, Fe, Ni, Zn, Mg, Cr, V, Cd, Cu, Pb)*

Site comparison



Size fraction comparison



Enrichment factor calculations

To establish the presence of a given trace element from anthropogenic origin the enrichment factor (EF) values were calculated. Fe was chosen as the reference element. The EF of an element X is defined as

EFx = (X/E)Air PM sample/ (X/E)crustal

Where E is the reference element. The average continental crust given by Taylor and McLennan (1) was selected as the crustal profile. The elements that have EF values between 1 and 10 are usually termed as crustal, while elements with EF values in the range 10 to 50,000 are generally emitted by anthropogenic sources

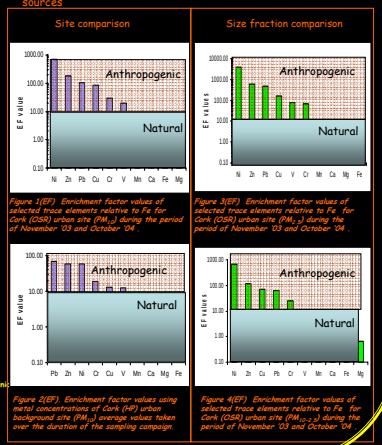


Figure 1(EF). Enrichment factor values of selected trace elements relative to Fe for Cork (OSR) urban site (PM_{10}) during the period of November '03 and October '04.

Figure 3(EF). Enrichment factor values of selected trace elements relative to Fe for Cork (OSR) urban site ($PM_{2.5}$) during the period of November '03 and October '04.

Figure 2(EF). Enrichment factor values using metal concentrations of Cork (HP) urban background site (PM_{10}) average values taken over the duration of the sampling campaign.

Figure 4(EF) Enrichment factor values of selected trace elements relative to Fe for Cork (OSR) urban site ($PM_{10-2.5}$) during the period of November '03 and October '04

2005 - 2006 SAMPLING CAMPAIGN

Sampling Location

3 Sampling sites

- Urban roadside site (OSR)
- Urban background site (HP)
- Rural background "clean air site" (Iniscarra)

Sampling equipment

Samples are collected using a high volume cascade impactor (Fig 2). Monitoring coarse (PM10-2.5) and fine (PM2.5) fractions.

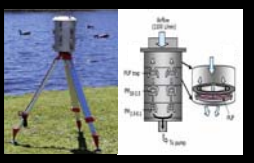


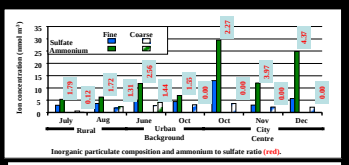
Fig 1(S). The three stage high volume cascade impactor, collecting $PM_{10-2.5}$ and $PM_{2.5}$ onto polyurethane foam.

- High flow rate of 900 l min^{-1}
- Uses polyurethane foam an inert collection substrate
- High weight of PM can be collected in a short period of time, providing an excess of sample for chemical analyses and sufficient weight for toxicological studies

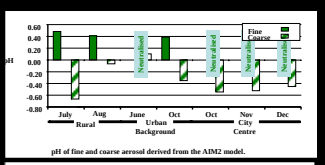
RESULTS & DISCUSSION

Inorganic ions

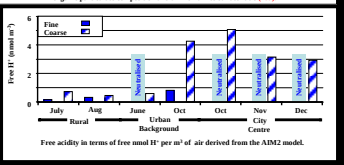
Post collection, the samples were conditioned for one week in a dessicator and the samples re-weighed to obtain the dry particulate weight. Sections of the PUF were aqueous extracted and the extract filtered (0.22 µm pore size). The filtered samples were analysed for ammonium and sulfate ions using a 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).



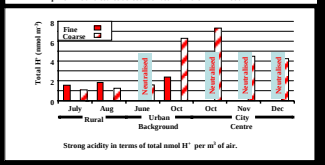
Inorganic particulate composition and ammonium to sulfate ratio (red).



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



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



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

Organics

PUF samples were subject to Soxhlet extraction and separated by sequential elution through a silica gel solid phase column. GC-MS was used to determine the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants.

Emission Source Markers:

- 3 and 4-ringed PAHs (e.g. Phe, Ant, Fla, Pyr) are usually associated with coal, oil and biomass combustion as well as with incineration processes.
- 5 and 6-ringed PAHs (e.g. BbF, BkF, BaP, DahAn) are usually associated with traffic combustion emissions from both gasoline and diesel fuel. 6-ringed PAHs (e.g. InPy, BghiPe) are more associated with diesel vehicles.

Fine Fraction Spatial Variability

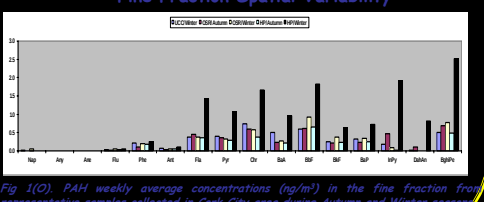
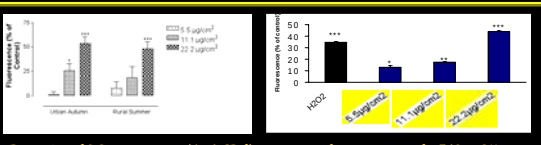


Fig 1(O). PAH weekly average concentrations (ng/m³) in the fine fraction from representative samples collected in Cork City area during Autumn and Winter seasons

Conclusions

- **Trace metals:** In relation to trace metal concentration, it can be concluded that Cork city is a low to moderately polluted European city. A large EF value for Ni was noted at the urban site (OSR) indicates that it contributes more to the anthropogenic emissions at this site.
- **Inorganic 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 (Hong Kong) but this calculation assumes that the water content of aerosol had a density of 1.
- **Organics:** Similar Total PAH concentrations were found in the fine fraction for the 3 sampling sites except for the winter sample from HP where the total concentration was three times bigger.
- **Toxicity study (ROS exp):** The preliminary results indicate that the particulate matter at the central urban site have a greater degree of bioreactivity. However at this stage the difference is not statistically significant. Further experimentation will investigate the seasonal difference in bioreactivity at the three study sites.

Toxicity studies (Preliminary investigations)



Formation of ROS as measured by DCF-fluorescence after exposure of A549 to $PM_{2.5}$ sampled in Cork urban area. Exposure time was 72 h at increasing concentrations of $PM_{2.5}$ (5.5, 11.1, 22µg/cm²) with results reported as the % of control values. H_2O_2 exposed cells are used as positive controls. These values are depicted as mean values of 6 replicates for controls, positive controls and every PM concentrations. (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$)