Linking urban field measurements to their chemical analysis and their effects on health

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Introduction

Epidemiological research has highlighted the detrimental effects of airborne particulate matter (PM) on human health. However there is still a wide debate over which characteristics of PM are responsible for the adverse health effects. The sources of PM are fairly well understood but their trace element composition and mechanism by which they exert their toxic effects still remains unclear. To a first approximation, the smaller the particle the further it will penetrate the lung so the greater the toxicity.

PM is generally classified by two factors: SIZE and (more recently) CHEMICAL COMPOSITION.

The size classification is as follows: **PM_{10}** (particulate matter with a diameter less than 10 µm) and **$PM_{2.5}$** (that less than 2.5 µm). Chemical analysis shows PM to comprise many inorganic, 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. Hence the necessity for integrated collection/analysis/toxicology projects of the type described here.

Aims

- Collection of $PM_{10-2.5}$ and $PM_{2.5}$ in Cork (Roadside, Urban Background and Rural sites)
- "Total" physico-chemical analysis method development to determine composition

THIS WILL LEAD TO:

- *Characterization* of ambient particulate matter and related species for the determination of source receptor relationships and also atmospheric processing pathways.
- *Data retrieval* from the total chemical analysis to develop a Computer Model for determining the origin & distribution of PM in Cork.
- *Determination* of biochemical/toxicological effects for airborne particulate components.

Experimental

Field Measurement:

Samples are collected using two types of samplers, the high volume cascade impactor (Fig 1) and the dichotomous Partisol sampler (Fig 2). Both can monitor for the coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) fractions.

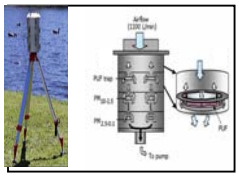


Fig 1. The three stage high volume cascade impactor, collecting $PM_{10-2.5}$ and $PM_{2.5}$ onto polyurethane foam.

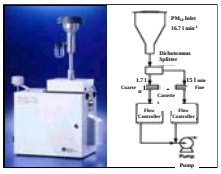
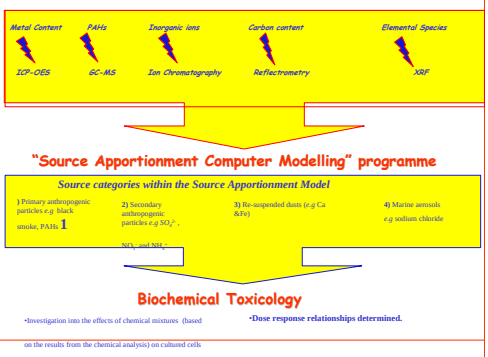


Fig 2. The Partisol sampler with the dichotomous splitter for the collection of $PM_{10-2.5}$ and $PM_{2.5}$ on PTFE filters.

- High flow rate of 1100 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

- 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 flourescence.

Total Chemical Analysis:



Results

Aerosol Acidity

Relative indicator of the acidity of aerosols

- Primarily associated with fine particles
- $[NH_4^+]/[SO_4^{2-}]$ ratio (Ion chromatography) is an indication of the degree of neutralization of the droplets
- When $[NH_4^+]/[SO_4^{2-}] > 2$ completely neutralized particles
- Categorized into

1) Ammonium rich particles (AR) (2> $[NH_4^+]/[SO_4^{2-}]$>1.5)

These (AR) particles are mostly neutralized with little free acid

2) Ammonium poor particles (AP) ($[NH_4^+]/[SO_4^{2-}]$<1.5

AP particles have a significant amount of free acid

Strong Acidity

- In terms of nmol H^+ per m^3 of air primarily associated with fine particles
- The total H^+ from strong acids in aqueous extract of atmospheric samples therefore can not give the in situ characteristics of atmospheric aerosols
- Estimated using an ionic balance of the inorganic ionic species
- In AP samples (Ammonium poor) strong acidity can be estimated as:

$[H^+] = 2[SO_4^{2-}] - [NH_4^+]$

- In AR samples (Ammonium rich):

$[H^+] = [SO_4^{2-}] + [SO_4^{2-}] \times ([NH_4^+]/[SO_4^{2-}] - 1.5) - [NH_4^+]$

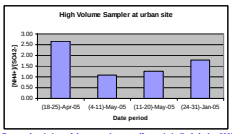


Fig a.Temporal variations of the ammonium-to-sulfate ratio in Cork during 2005, sample taken from High volume sampler

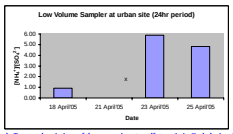


Fig b. Temporal variations of the ammonium-to-sulfate ratio in Cork during April 2005, sample taken from low volume sampler

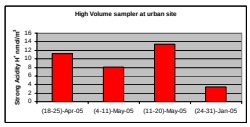


Fig c. Temporal variations of the strong acidity in Cork during 2005, sample taken from high volume sampler

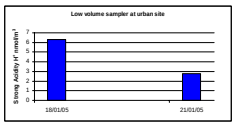


Fig d. Temporal variations of the strong acidity in Cork during April 2005, sample taken from low volume sampler

Trace elements

ICP-OES analysis:

*Metals analysed are: Ca, Mn, Fe, Ni, Zn, Mg, Cr, V, Cd, Cu, **Pb**, As, Ti, Al, Si*

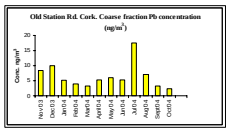


Fig e Monthly-average view of Old Station Road (Coarse fraction)

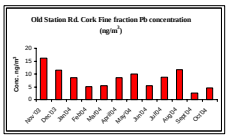


Fig f Monthly-average view of Old Station Road (Fine fraction)

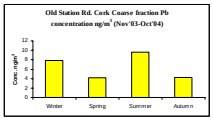


Fig g Seasonal-average view of Old Station Road Coarse fraction

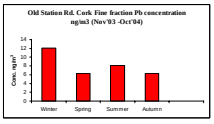


Fig h Seasonal-average view of Old Station Road Fine fraction

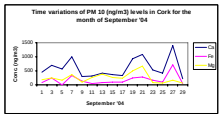


Fig k PM_{10} trace elements of a crustal origin. Taken from a background urban site in Cork using a low-volume Partisol sampler.

Enrichment factor

- Determination of the contribution of anthhropgenic emissions to atmospheric elemental levels
- Defined as: EF =(E/R)air / (E/R)crust

where R=reference element (Fe) and E=element.

- EF is close to unity ⟶ crustal is the predominant source

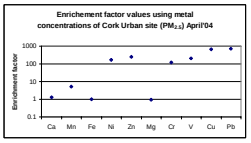


Fig i Enrichment factor values using the metal concentrations of Cork sampling for the month of April 05

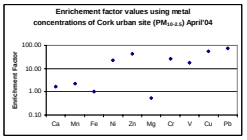


Fig j Enrichment factor values using the metal concentrations of Cork sampling for the month of April 05 $PM_{10-2.5}$

- The sequence of EF in Cork (Urban site) was:
- For $PM_{10-2.5}$: Pb>Cu>Zn>Cr>Ni>V>Mn>Ca>Fe>Mg

and for $PM_{2.5}$:Pb>Cu>Zn>Ni>V>Cr>Mn>Ca>Fe>Mg

Conclusions

- **Concluding on the quality of Cork air from an inorganic point of view, it could be said that Cork is a low to moderately polluted city.**
- **For Pb metal concentrations none of the monthly analyses exceeds 18ng m^{-3}. No monthly value was found to be less than 2 ng m^{-3}.**
- **Analysis of the seasonal trends at Cork indicates that a greater Pb concentration is found in the fine fraction (by a factor of some 50%) except in Summer when the coarse and fine fractions appear to be similarly loaded. This latter observation is driven by a comparatively high Pb concentration measurement made in July 2004 for the Cork $PM_{10-2.5}$ fraction.**
- **The seasonal trends also indicate a greater Pb concentration in the Autumn/Winter pair compared to the Spring/Summer pair for the OSR $PM_{2.5}$ fraction.**
- **The levels of Pb detected in the above campaign are comparable to measurements previously reported for OSR Cork.**
- **The measurements represent the first analyses comparing Pb (and the other metals listed above) content in coarse and fine PM fractions in Cork.**
- **The annual average concentration of Pb for the urban background site was found to be well below the EU limit thhreshhold values over the twelve-month period (PM_{10} twelve month average for Pb =14.65ng/m^3). Furthermore concentrations of Ni and Cd were lower than the prospective assessment thresholds at all sites and As concentrations were found to be below the detection limits in all samples.**
- **The ammonium-to-sulfate ratio ($[NH_4^+]/[SO_4^{2-}]$) results showed that for 23-Jan-05 and 25-Jan-05 (results taken from the low volume sampler figure b results), to be greater than 2 so were considered to be completely neutralized and have zero strong acidity as shown in Fig d.**
- **The enrichment factor values shown in fig i and j suggests that the elements Ni, Zn, Cr, V, Cu and Pb originate from a non crustal sources with anthropogenic sources dominating their release into the ambient air *e.g.*pollution emissions, traffic related emissions and incineration etc.**
- **Where as for the elements Ca, Mn, Fe, and Mg these have enrichment factor values close to unity, therefore crustal origin is the predominant source. This is also in agreement with fig k where it is shown for the month of September that these elements follow a similar time trend.**

Future Work

- The ammonium-to-sulfate ratio ($[NH_4^+]/[SO_4^{2-}]$) and the strong acidity do not provide the insitu acidic characteristics of atmospheric aerosols, therefore more investigations need to be carried out into the pH of the aerosols and the free acid concentrations

Acknowledgements

- **Dr A. Whittaker, Dr J. Lopez, Dr J Wenger and Prof. J. Sodeau**
- **Cork City Council, Ireland.**
- **Environmental protection agency of Ireland RTDI Doctoral Scholarship Programme**

References

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