

## INTRODUCTION

Particulate matter (PM) in urban air consists of a complex mixture of primary and secondary emissions from both anthropogenic and biogenic sources. Airborne particulates are typically comprised of a large number of ionic, organic and metallic species that are able to penetrate deep into the respiratory system and are known to have an adverse effect on human health (Pope *et al.*, 2002). Some of these adverse health effects are due in part to oxidative stress which can be caused by the generation of excess Reactive Oxygen Species (ROS) such as the superoxide ion radical. ROS generation can be catalyzed by organic species such as quinones (Kumagai *et al.* 2002). In Ireland, approximately one third of PM<sub>2.5</sub> in urban areas is attributed to the organic fraction (Yin *et al.*, 2005). The assay used in this study is specific for the organic fraction and is based on the ability of organic constituents such as quinones which are present on PM to catalyze the reduction of oxygen by DTT which is added in excess. Temporal and spatial trends with ROS activity and correlations with quinone and Polycyclic Aromatic Hydrocarbon (PAH) concentrations were examined.

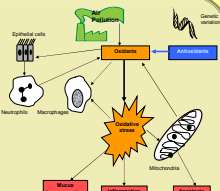


Fig 2. Oxidative stress and its effects adopted from Wood and Stockley. Oxidants in ambient air trigger epithelial cells and macrophages and respond with more cell-generated oxidants. Oxidative stress is a result of an imbalance occurring where the rate of formation of ROS exceeds the capacity of antioxidant systems, causing effects such as apoptosis.

## 2005-2006 SAMPLING CAMPAIGN



Fig 3. The three stage high volume cascade impactor, collecting PM<sub>10-2.5</sub> and PM<sub>2.5</sub> onto polyurethane foam.

The HVCI (Fig. 3) with a flow rate of 900 L min<sup>-1</sup> enables a large volume of PM to be collected over a relatively short period of time. Polyurethane foam (PUF) was used to collect the substrate. PUF is a chemically inert material that can hold a large weight of PM (up to 2g cm<sup>-2</sup>). Weekly samples were collected from January 2005 to December 2006. The results shown here are from PM collected at Inishcarra (rural background), Old station Road (city site) and Heaherton Park (urban background site UBS).

PUF samples are extracted as illustrated in Fig 4.

A sample from each site/season is then added to a 250 mM Tris-HCl buffer adjusted to pH of 8.9 with KOH at 37 °C containing 16mM DTT. The solutions are incubated for 10 minutes to allow sufficient time for the catalysis of the DTT sulphydryl oxidation to occur. 32 mM DTNB is added to develop the colour and the absorbances read at 414 nm to ascertain the ROS activity.

Samples are treated with a derivatising agent (acetic anhydride and zinc catalyst) which reduces the polarity and increases volatility which is required for GCMS. Samples are analysed using GC-MS (30 m x 0.25 mm x 0.25 µm capillary column) with a flow rate of 1.0 ml min<sup>-1</sup> and a gradient temperature profile. The MS qualification parameters are illustrated in Table 1.

The PAHs in ambient samples are Soxhlet extracted and separated by flash chromatography (Fig 5). These extracts are analysed using GC-MS, with a flow rate of 1.5 ml min<sup>-1</sup> and a gradient temperature profile. The MS qualification parameters are illustrated in Table 2.



Fig 1. Location of field sampling campaign in Cork, Ireland

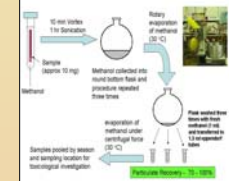


Fig 4. PM sample extraction process

Quinone Name	Retention time (minutes)	Characteristic M/Z
Hydroquinone (IS)	18.75	166.1, 208.1, 250.1
1,2 naphthoquinone	23.21	160.1, 202.0, 244.0
1,4 naphthoquinone	24.36	160.1, 202.0, 244.0
9,10 benzoanthraquinone	33.35	210.1, 252.0, 294.0
9,10 anthraquinone	33.69	210.1, 252.0, 294.0

Table 1. Qualification parameters for the identification of derivatised quinones using Single Ion Monitoring (Agilent GC-MS 5973 with mass selective detector)

Polycyclic Aromatic Hydrocarbons	Characteristic M/Z	Ion Preparation
Naphthalene	102	MS/MS
Acenaphthylene	150-152	MRM
Acenaphthene	150	MRM
Fluorene	163	MS/MS
Phenanthrene	152, 176	MS/MS
Anthracene	152, 176	MS/MS
Fluoranthene	200	MS/MS
Pyrene	200	MS/MS
Chrysene	226	MS/MS
Benzo(A)Anthracene	226, 226	MS/MS
Benzo(B)Fluoranthene	249, 250	MS/MS
Benzo(K)Fluoranthene	249, 250	MS/MS
Benzo(A)Pyrene	249, 250	MS/MS
Indeno(1,2,3)Pyrene	272, 274	MRM
Dibenz(A,H)Anthracene	272, 274	MRM
Benzo(G,H,I)Perylene	272	MS/MS

Table 2. PAH GC-MS Qualification parameters

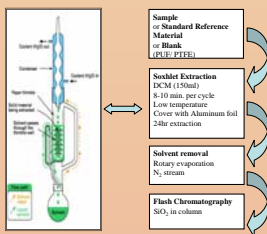


Fig 5. PM sample extraction process for PAHs

## RESULTS

### Redox Activity and Spatial and Seasonal Variation

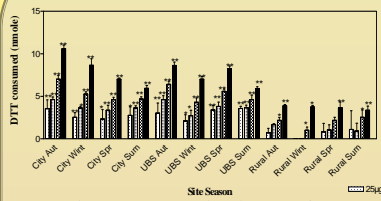


Fig 6. Redox activity is expressed as the amount of DTT consumed. Redox activity is plotted as a function of site and season to facilitate the presentation of Spatial and Season variations. Significance between samples and control was determined by ANOVA, Dunnett's post test (n=4)

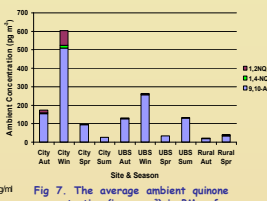


Fig 7. The average ambient quinone concentration (in pg m<sup>-3</sup>) in PM<sub>2.5</sub> for the various locations around Cork Ireland. These values are based on single representative samples that were analysed by GC-MS triplicate injections

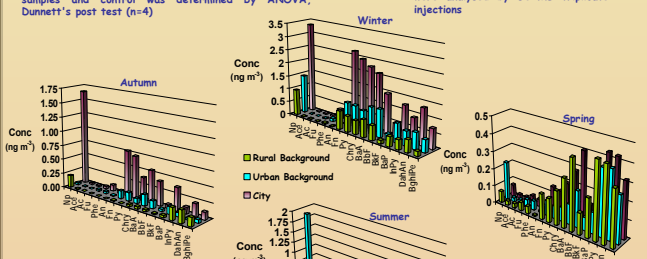


Fig 8. Average individual PAH Concentrations as a function of site and season during the 2005-2006 campaign. The number of site/season samples varies from n=2 to n=7. The concentration of naphthalene seems elevated when compared with other low molecular weight PAHs. PUF substrate is known to trap gases and this may explain this elevated concentrations.

ROS Activity (nmoles DTT consumed) (min)	Concentration of Organic Species (site/season averages)																
100 µg m <sup>-3</sup>	Total Quinones	Np	Ac	Ac	Fu	Phe	An	Flu	Py	Chry	Ben	BbF	BbF	BaP	Indy	DahAn	BghiPe
200 µg m <sup>-3</sup>	0.4313	0.42	0.43	0.36	0.61	0.49	0.56	0.41	0.42	0.34	0.37	0.34	0.31	0.409	0.169	0.242	0.275

Table 3. Table of correlation coefficients (Pearson Coefficient R) corresponding to the concentration of measured quinones and PAHs as a function of ROS activity for site-season specific samples in this study

## DISCUSSION

### Quinone and PAH Concentration:

### ROS Activity:

- > Across all sites and seasons 9,10-Anthraquinone (9,10-AQ) contributed the most to the quinone concentration. This is in line with other studies that report 9,10-AQ as being the largest quinone contributor found in diesel exhaust
- > Naphthoquinones (NQs) are directly emitted by motor vehicles. In a study conducted by Jakober C. A. et al, the measured particle phase emission rate of 1,2-NQ > 1,4-NQ species for heavy-duty diesel vehicles.
- > The city site is located adjacent to a major traffic artery into the city and the highest concentrations were recorded at this site during the winter and autumn.
- > Excluding naphthalene, the highest PAHs concentrations were observed during winter at the city site. 4-Ringed Fluoranthene, Pyrene and Chrysene are emitted from incomplete combustion processes. At the urban background site, Benzo(B)Fluoranthene, a 5-ringed PAH registered the highest concentration. 5-ringed PAHs are indicative of petrogenic emissions.
- > The urban locations during the autumn season generated the largest assay response followed closely by the response recorded by the winter urban samples.
- > This maybe due to the increase in heating emissions and lower temperatures associated with the autumn and winter months.
- > The rural site presented a consistent response throughout the seasons with little seasonal variation and provided lowest response recorded for each season across the 3 sites.
- > The main quinone species found in the ambient samples are associated with vehicular (primary) emissions sources
- > 3 and 4-ringed PAHs (e.g. Fu, Phe, An) are usually associated with coal, oil and biomass combustion as well as with incineration processes. These PAHs showed the highest correlation with the ROS activity results.

## CONCLUSIONS & FUTURE WORK

- > ROS activity at its highest in the Autumn/Winter Months
- > Increased combustion processes during these months (coal and oil) and vehicular cold-starts. The atmospheric loss processes for organic species are less efficient in the low sunlight conditions of autumn and winter. Winter meteorological conditions such as temperature inversion also favour less pollutant dispersion.
- > Low molecular weight PAHs appear at very low concentrations compared with the high molecular weight PAHs.
- > The extent of partitioning between gas and solid-phase strongly depends on PAH volatility, temperature and the amount of available surface material.
- > Main PAH and Quinone sources are combustion processes (coal, oil, biomass), incineration and traffic emissions.

Principal Component Analysis will be carried out in order to provide more detailed information of the possible emission sources in the Cork urban area.

## ACKNOWLEDGEMENTS

Authors wish to thank the following bodies for their financial assistance:

- > IRCSET Embark Initiative
- > 6th Framework Program Marie Curie TOK Actions
- > Irish EPA

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