

SPATIAL AND TEMPORAL VARIABILITY OF PAH CONCENTRATION IN CORK URBAN AIR.

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INTRODUCTION

According to the World Health Organization, 4-8% of deaths occurring annually in the world are related to air pollution. The main pollution sources are associated with anthropogenic activities and the emission of gases and particulate matter. The particles are generally classified by their size rather than composition. Thus "coarse" particles have aerodynamic diameters larger than 2.5 µm and "fine" particles possess diameters lower than 2.5µm. Particulate matter can contain a wide range of chemical species ranging from elements (e.g. carbon, trace metals, silicon) to inorganic ions (e.g. nitrate, sulphate) and organic compounds such as polycyclic aromatic hydrocarbons (PAHs). PAHs are of particular concern because of their carcinogenic and mutagenic properties. Within this context, the purpose of this study is to assess the spatial and temporal variability of PAH concentration in Cork urban air by measurements obtained from two different sampling campaigns in 2001 and 2005. The samples were collected using two types of samplers, a high volume cascade impactor (HVCI) and a dichotomous Partisol sampler. Both samplers separate the collected PM10 into the coarse (PM10-2.5) and fine (PM2.5-0.1) fractions. Three locations were chosen for the sampling programme including the city centre, a "background urban" site and a "background rural" site. Soxhlet extraction followed by sequential elution through a silica gel solid phase extraction column and gas chromatography-mass spectrometry (GC-MS) has been used to analyse a range of organic compounds including Polycyclic Aromatic Hydrocarbons (PAHs).

2001-2002 SAMPLING CAMPAIGN

EXPERIMENTAL

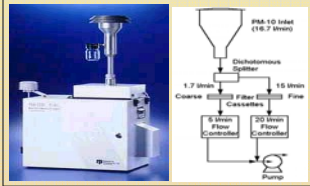


Fig. 1. The Partisol sampler with the dichotomous splitter for the collection of PM10-2.5 and PM2.5 on PTFE filters.

The R&P Dichotomous Partisol-Plus Model 2025 Air Sampler (Fig. 1) contains a virtual impactor and flow controllers located in the inlet line. These controllers separate the flow into 15.0 L min⁻¹ and 1.7 L min⁻¹ for the fine and coarse fraction respectively. 24-hour samples were collected onto 47mm diameter Whatman PTFE filters for alternate days. Sampling was conducted at the Cork City Centre Old Station Road site (OSR) on alternate days from September 2001 - October 2002. Filter samples were subject to Soxhlet extraction with 150 ml of dichloromethane for 18 hours and analysed by GC-MS to determine the concentrations of the 16 PAHs listed by the US-EPA as priority pollutants.

RESULTS AND DISCUSSION

Coarse Fraction Seasonal Trend

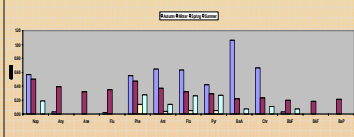


Fig. 2. PAH seasonal average concentration (ng/m³) in the coarse fraction. Samples collected at OSR Cork City Centre.

Fine Fraction Seasonal Trend

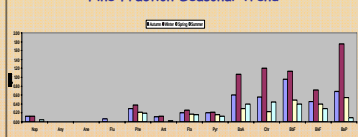


Fig. 3. PAH seasonal average concentration (ng/m³) in the fine fraction. Samples collected at OSR Cork City Centre.

Temporal variability:

The mean concentrations in the autumn and winter months were significantly higher than those in the summer months. The difference has been attributed to:

- Increase in emissions from domestic heating.
- Winter traffic (from congestion and cold starts).
- Meteorological conditions which favour less pollutant dispersion in winter.
- Possible loss of PAHs due to photochemical reactions in summer.

CONCLUSIONS & FUTURE WORK

➢ Majority of PAHs are found in the fine fraction. PAHs mainly originate from incomplete combustion processes of anthropogenic origin which are characterised by particle emissions mostly in the fine fraction.

➢ 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.

➢ There is a seasonal trend with higher PAH emissions during Winter and Autumn.

➢ Main PAH sources are combustion processes (coal, oil, biomass), incineration and traffic emissions.

➢ It is necessary to extend the 2005-2006 sampling campaign and analyses in order to complete temporal and spatial variability studies.

➢ This study will be extended to include additional organic compounds; alkanes, aldehydes and ketones.

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

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2005-2006 SAMPLING CAMPAIGN

EXPERIMENTAL

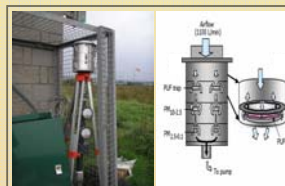


Fig. 4. The three stage high volume cascade impactor, collecting PM10-2.5 and PM2.5 onto polyurethane foam.

The HVCI (Fig. 4) with a flow rate of 900 L min⁻¹ 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⁻²). Weekly samples have been collected since January 2005. The results shown here are from PM collected at UCC (University College Cork), OSR (City Centre) and Heatherton Park (HP, background urban). 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.

RESULTS AND DISCUSSION

Fine Fraction Spatial Variability

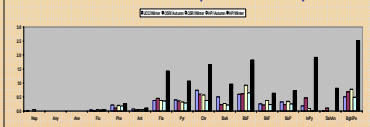


Fig. 5. PAH weekly average concentrations (ng/m³) in the fine fraction from representative samples collected in Cork City area during Autumn and Winter seasons.

➢ 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.

	Autumn	Winter
UCC		4.23
City Centre	4.16	4.41
Landfill	3.16	13.9

Table 1. Fine fraction Total PAH concentration (ng/m³).

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.

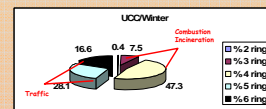


Fig. 7. Fine fraction PAH distribution by number of rings and potential emission sources, UCC Winter.

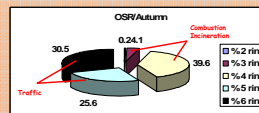


Fig. 8. Fine fraction PAH distribution by number of rings and potential emission sources, OSR Autumn.

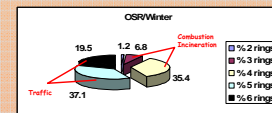


Fig. 9. Fine fraction PAH distribution by number of rings and potential emission sources, OSR Winter.

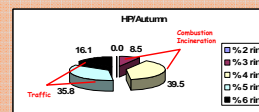


Fig. 10. Fine fraction PAH distribution by number of rings and potential emission sources, HP Autumn.

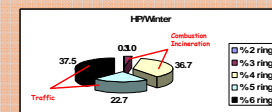


Fig. 11. Fine fraction PAH distribution by number of rings and potential emission sources, HP Winter.

➢ Contribution sources are almost equally divided between combustion (45%) and traffic (55%) in the Cork City urban area.

➢ UCC/Winter sample shows a higher contribution related with combustion (55%).

➢ HP/Winter sample shows a higher traffic contribution (60%).