

## Organic Composition of PM<sub>2.5</sub> Aerosols in Cork Harbour, Ireland

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Atmospheric particles with diameters less than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>) have adverse effects on human health, visibility and climate. A substantial fraction (20-90%) of atmospheric fine particulate matter are comprised of organic compounds (Kanakidou *et al.*, 2005), which cover a wide range of polarities, volatilities and masses. Our knowledge on the organic chemical composition of atmospheric aerosols is rather limited; only about 30% of the organic matter has been characterised at the molecular level. Nevertheless, some of the identified compounds are source specific and can provide important information on aerosol sources and source processes.

In this study, PM<sub>2.5</sub> aerosol samples were collected during summer and autumn 2008 periods in the Tivoli Industrial and Dock Estate (Cork, Ireland). The sampling site is characterised as a very complex environment supporting a variety of industrial and domestic activities and representing many emission sources. Aerosol samples were analysed for non-polar and polar organic compounds that are useful markers for the aerosol source characterisation. Non polar organic compounds were determined using thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) and included polycyclic aromatic hydrocarbons (PAHs) and n-alkanes (C<sub>20</sub>-C<sub>30</sub>). The carbon preference index (odd to even ratio) of identified n-alkanes corresponded to diesel and smoke emissions and was comparable with those reported from other urban areas. Major PAHs included naphthalene, acenaphthylene, acenaphthene, phenanthrene, fluoranthene, and pyrene. All detected PAHs are of major health concern due to their well-known carcinogenic and mutagenic properties.

Polar compounds were determined with GC/MS after extraction with CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> mixtures and a derivatization process that converts carboxylic and hydroxylic groups of the organic compounds to trimethylsilyl (TMS) derivatives. Major polar compounds identified in the summer samples were oxidation products of isoprene, including the 2-methyltetrols and C<sub>5</sub> alkene triols. Other identified water-soluble compounds were: malic acid, levoglucosan, galactosan, mannosan, glyceric acid, arabitol and mannitol. Of the latter compounds, galactosan and mannosan are markers for biomass burning that are formed during the pyrolysis of cellulose at temperatures >300°C. Levoglucosan is another biomass burning marker that is formed during combustion and found in both cellulose and lignite pyrolysates (Fabbri *et al.*, 2008).

Arabitol and mannitol are markers for fungal spores, while the origins of malic acid and glyceric acid are still not clear. During the autumn and late autumn periods the atmospheric concentrations of the isoprene oxidation products, as well as the markers for fungal spores, decreased to undetectable levels. This observation can be explained by the occurrence of colder temperatures and lower photochemical activity. In contrast, the average concentrations of biomass burning markers (levoglucosan, mannosan and galactosan) increased substantially from 10 ng/m<sup>3</sup> during summer to 116 ng/m<sup>3</sup> (reaching up to 550 ng/m<sup>3</sup>) during the late autumn period. For the late autumn campaign, biomass burning markers exhibited diel variations with the highest concentrations during night-time. The regression analysis demonstrated excellent correlation (R<sup>2</sup>>0.99) between galactosan, mannosan and levoglucosan concentrations suggesting that the main source of the biomass burning is cellulose-containing solid fuel (e.g., firewood or peat).

The contributions of different aerosol sources to the organic carbon (OC) mass were assessed based on the available source profile data and average concentrations of the detected polar organic compounds. The average atmospheric concentration of wood smoke was estimated at 59 ng C/m<sup>3</sup> (or 5.5% of the OC) during the summer period and increased up to 650 ng C/m<sup>3</sup> (or 28.5% of the OC) during the late autumn period. During the summer campaign the average atmospheric concentration of fungal spores was 11 ng C/m<sup>3</sup>, which corresponds to 1% of the OC, while that of isoprene SOA was estimated at 19.5 ng C/m<sup>3</sup> and 1.8% of the OC.

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