

Molecular composition of PM_{2.5} aerosols from Cork Harbour, Ireland using ultrahigh resolution mass spectrometry

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Aerosol particles have a profound effect on the radiative balance of the atmosphere and human health (Kanakidou et al., 2005). Organic compounds are important constituents of fine particulate matter in the troposphere; however, due to the complexity of the aerosol matrix, their comprehensive analysis at a molecular level is a long standing issue. In this study, we applied direct infusion nano-electrospray (nanoESI) ultrahigh resolution mass spectrometry (UHR-MS), which allows the determination of hundreds of individual constituents at once (Nizkorodov et al., 2011), for the analysis of ten PM_{2.5} aerosol samples collected from Tivoli Industrial and Dock Estate (Cork, Ireland) during 9-17 September, 2011.

All aerosol samples were analysed for organic carbon (OC) and elemental carbon (EC) using a thermal optical transmittance (TOT) technique. Depending on the OC load of the aerosol sample, a portion of the filter was extracted in methanol, filtered, and reduced by volume to approximately 100 µL. The extracts were analysed using an LTQ Orbitrap Velos MS fitted with a chip-based electrospray ion source, TriVersa NanoMate®. The mass spectra were recorded in negative mode over the mass ranges m/z 100-650 and 150-900 with a mass resolving power of 100,000 ($m/\Delta m$) at m/z 400. Background peaks were subsequently eliminated by subtraction of peaks present in blank samples. The remaining peaks were assigned probable empirical formulae applying several conservative rules and constraints (e.g., valence rule, double bond equivalent, isotopic ratios) and assuming that ions contain only ¹²C, ¹³C, ¹H, ¹⁶O, ¹⁴N, ³²S, and ³⁴S. In addition, selected samples were screened for organic acids and organosulphates using liquid chromatography LC/ESI-qTOF MS.

Depending on the sample, 400-640 elemental formulae were identified using direct infusion UHR-MS and attributed to organic species with molecular weights below 450 Da. The assigned formulae were grouped into four subgroups: CHO, CHOS, CHON and CHONS with CHO (average 63% of the total formulae) being the most frequently apportioned subgroup, followed by CHON (25%), CHOS (9%), and CHONS (3%). A rather large number of identified organonitrates indicates anthropogenic influence on the aerosol composition at

Tivoli Industrial and Dock Estate site. O/C and H/C ratios of the aerosols were on average 0.45 and 1.3, respectively and remained constant throughout the sampling period.

Kendrick Mass Defect and Van Krevelen approaches were used to identify compound classes and mass distributions of the detected species. A very high number of aromatic like compounds that typically have low H/C (≤ 1.0) and O/C ratios (≤ 0.5) and aliphatic compounds with high H/C ratios (≥ 1.5) and low O/C ratios (≤ 0.5) were observed in all samples. These findings suggest that the sampling site is affected by both anthropogenic and biogenic activities. The majority of the species had carbon oxidation state (OSc) between -1.5 and +1 with 20 or less carbon atoms, suggesting that they are semi- and low-volatile organic compounds corresponding to both 'fresh' and 'aged' aerosol produced by multistep oxidation reactions. A very large fraction of ions had OSc < -1 that is characteristic for primary biomass burning aerosol, indicating that even during summer burning of domestic fuel material is important.

LC/MS analysis of the aerosol samples allowed identification of a few dicarboxylic acids and organosulphates which possibly originated from combined anthropogenic and biogenic sources. The results of this work demonstrate that the studied site is a very complex environment affected by a variety of industrial and domestic activities and natural sources, which is reflected by the unique aerosol composition representing many emission sources.

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Kanakidou, M., Seinfeld, J. H., Pandis, Barnes, I., Dentener, F. J., Facchini, M. C., van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., et al. (2005). *Atmos. Chem. Phys.*, **5**, 1053-1123.

Nizkorodov, S.A., Laskin, J., and Laskin, A. (2011). *Phys. Chem. Chem. Phys.*, **13**, 3612-3629.