



# Real-time Measurements of Single Particle Composition at Cork Harbour, Ireland



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## Introduction

Although many studies investigating the chemical composition of individual particles have been performed in various remote and urban environments, in-port sites have received comparatively little attention. Emissions from shipping traffic in particular remain relatively unconstrained and may impact severely upon local and regional air quality and health in port cities [1]. The focus of this campaign was to investigate the internal and external mixing state of ambient particles in Cork Harbour, Ireland, with particular interest in the contribution from ship exhaust. A TSI 3800 aerosol time-of-flight mass spectrometer (ATOFMS) was co-located with a suite of real-time instrumentation at an in-port site for three weeks in August 2008. Over 500,000 positive and negative ion particle mass spectra were generated and divided into various classes using the K-means algorithm [2]. Approximately 2.5% by number of the particles observed were apportioned to ship exhaust, exhibiting composition in line with recent in situ ship exhaust measurements [3]. The vast majority of these particles lie in the ultrafine mode and thus are expected to have human health implications. Furthermore, 2.5% by number is considered to be very much a lower limit as the majority of the particles lie below the measurable size range of the aerodynamic lens of the ATOFMS.

[1] Lubick, N. *Environ. Sci. Technol.* **2007**, 41, 8206-8211 [2] MacQueen, J. *Fifth Berkeley Symposium on Mathematical Statistics and Probability* **1967**, 1, 281 [3] Murphy, S. et al. *Environ. Sci. Technol.* **2009**, available on web, DOI: 10.1021/es802413j

## Sampling Site & Instrumentation



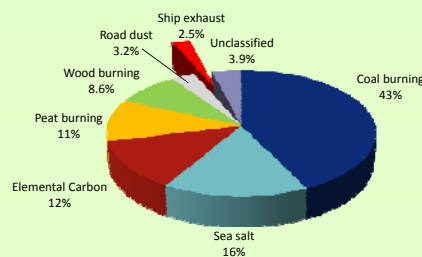
Location of the sampling site

ATOFMS and SMPS co-located on-site

The sampling site at the Tivoli Docks, Cork Harbour was chosen based on its position northeast of the port terminal and shipping berths. The prevailing winds are southwesterly and the closest berth is located 200 m to the southwest of the site. The ATOFMS and SMPS (scanning mobility particle sizer, TSI 3081) instruments were located in an adapted temperature-controlled truck. The ATOFMS was fitted with an aerodynamic lens (TSI AFL100) for the measurement of particles in the size range 100-3000 nm in real time. Particles are sized using two orthogonally positioned continuous wave lasers and ionized using a Nd:YAG laser (266 nm). The resulting positive and negative ions are then analysed using two time-of-flight mass spectrometers. The SMPS collected particle number concentrations and size distributions in the range 20-600 nm every 3 min. A TEOM (tapered element oscillating microbalance, Thermo model 1400) was also located on-site for the measurement of PM<sub>2.5</sub> mass concentration averaged every 30 min. Wind speed, wind direction, temperature, humidity and rainfall were measured using a Casella NOMAD weather station. The instruments were located on site for three weeks from 07-28/08/2008.

## Single Particle Composition

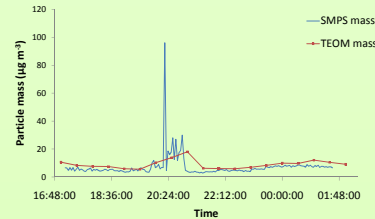
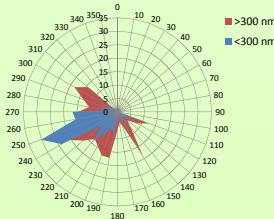
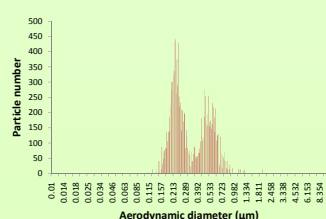
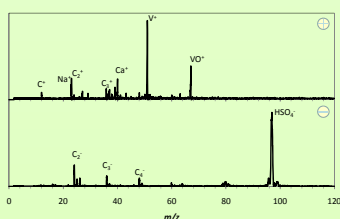
558,740 mass spectra were generated by the ATOFMS during the three week campaign. These spectra were initially reduced to 50 classes using the K-means algorithm [2]. Those 50 classes were further reduced to seven main particle types based on the similarity of their temporal trends, size distributions and mass spectra. Standard spectra for coal, peat and wood smoke were collected during a separate experiment by burning each fuel in turn and analysing the resulting particles.



Population of each particle class as a fraction of the total number of particles ionized by the ATOFMS

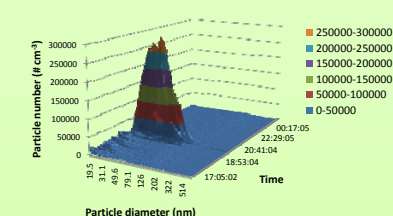
The largest contribution by number to the particles observed was domestic heating, with particles attributed to coal, peat and wood burning accounting for 63% of the overall number. The temporal trend for the domestic heating particles peaked, as expected, from 19:00-22:00 every evening, with no obvious dependence on wind direction indicating a diffuse local source. Road dust exhibited a daily temporal trend consistent with traffic, while ship exhaust particles exhibited sharp temporal events.

## Shipping Particles



Positive and negative ion mass spectra for a typical ship exhaust particle (left), bimodal size distribution of ship exhaust particles (middle) and wind dependence for both ship exhaust particle modes (right)

Ship exhaust particles were characterised by the presence of internally mixed organic carbon, elemental carbon, vanadium, sodium, calcium and sulfate. Typically ships use bunker fuel (residual fuel) known to contain these metal impurities as well as sulfur [3]. The size distribution from the ATOFMS data is bimodal suggesting two possible sources. When separated, particles <300 nm exhibited a very strong dependence on southwesterly wind direction indicating freshly emitted particles from the nearby berth. Particles >300 nm exhibited a slightly more diffuse source, consistent with aged shipping particles. Although the PM<sub>2.5</sub> mass measured by the TEOM averaged every 30 min does not exhibit dramatic spikes, the estimated mass data from the SMPS (3 min averages, assuming a density of 1.2 g cm<sup>-3</sup>) exhibits sharp peaks that coincide with the ATOFMS temporal trends for ship exhaust particles. It can be seen from the SMPS data that the vast majority of ship plume particles are in the ultrafine mode, and are thus missed by the ATOFMS. Therefore the estimated contribution by number (2.5%) of shipping to the overall PM<sub>2.5</sub> particle number may be considered a lower limit.



TEOM and SMPS particle mass concentration (top) and SMPS particle number and size distribution for the evening of 26/08/2008

## Future Work and Acknowledgments

Although signature ATOFMS dual ion mass spectra have been obtained for ship exhaust, coal, peat and wood burning particles the ATOFMS aerodynamic lens used for this campaign precluded the determination of ultrafine particle composition. A second aerodynamic lens (TSI AFL30) can be used at the Tivoli Docks site to determine any compositional differences between ultrafine and accumulation mode particles from the same source. The fraction by number of particles measured by the ATOFMS for each class can not be used as a quantitative measurement. However, the ATOFMS temporal trends will be used together with other real-time data including PM<sub>2.5</sub>, NO<sub>x</sub>, ozone, SO<sub>2</sub>, sulfate and EC/OC mass concentrations for source apportionment. Positive matrix factorisation using all of the variables available will be performed in order to determine the contribution of each source to local air quality. Many thanks to the Environmental Protection Agency and the Higher Education Authority for providing the funding for this project as well as the Cork Port Authority and Cork City Council for their collaboration and valuable input.