Applications of Single Particle Mass Spectrometry in Urban Environments

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Overview

- Why study single particles?

- The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)

- Urban Case Study 1: Cork Harbour

- Urban Case Study 2: MEGAPOLI campaign Paris

- Summary
Why Study Particle Composition?

- Particulate matter can affect our air quality, health and climate

- Effective mitigation strategies require a knowledge of the sources that contribute to particulate matter

- Particulate matter is a complex mixture of a variety of chemical species

- Many of these species are produced by multiple sources and the relative impact of each source upon air quality can be difficult to assess
Single particle composition and mixing state

**Externally** mixed particles

**Internally** mixed particles

- Organic carbon
- Elemental carbon
- Sulphate
Bulk sampling

- Filter sampling often involves low time resolution (24 h)

- Enables determination of the overall particle bulk composition but all single particle information is lost

- Can be difficult to identify sources of particles using bulk results
ATOFMS- principles of operation

- TSI Model 3800
- Detects elemental carbon, organic carbon, metals, inorganic ions for single particles

- Provides size-resolved chemical composition in real time

- Allows determination of chemical mixing state (internal or external mixtures)

- Some mixing states are unique to specific sources - very useful for assessing relative impact on air quality
Case Study 1: Cork Harbour

Cork is one of the top ten cities to visit, Lonely Planet 2010!
Data Analysis

- Over 500,000 ATOFMS mass spectra collected for Cork Harbour

- Need to reduce dataset to a workable size

- Clustering algorithm used ($K$-means) to group particles based on the similarity of their mass spectra

- Then examine these groups or “classes” with respect to size, composition, temporality- identify potential sources
Ship exhaust particles characterized by a unique mixing state

Healy et al., Atmos. Environ. 2009
Ship exhaust particles

- High temporal resolution of ATOFMS very useful for short-lived events
Particle size distributions - wood burning
Home heating particles

- Observed 3 different home heating combustion particle classes

- Identity confirmed through combustion experiments

- Coal, peat and wood combustion particles detected in Cork Harbour

<table>
<thead>
<tr>
<th>Fuel:</th>
<th>Coal</th>
<th>Peat</th>
<th>Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marker ions:</td>
<td>$C_xH_y^+$, $SO_4^-$</td>
<td>$Na^+$, $C_xH_y^+$, $Cl^-$</td>
<td>$K^+$, $C_xH_yO_z^-$</td>
</tr>
</tbody>
</table>

*Healy et al., Atmos. Chem. Phys. 2010*
Home heating particles

- Daily maxima occur in the evening when open fires are lit for heating
Traffic particles

- Traffic particles exhibit double maximum at traffic rush hours
Particle sources in Cork Harbour

- Local anthropogenic sources have the largest contribution to particulate matter in Cork Harbour

- Although the shipping contribution is small, these particles are acidic and contain vanadium and nickel

- Despite a ban on the domestic combustion of coal (Clean Air Act 1995), home heating remains the dominant source of particulate matter in Cork City*

*Kourtchev et al., Sci. Tot. Environ. 2010
Case study 2 MEGAPOLI

Megacities: Emissions, urban, regional and Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation

MEGAPOLI objectives

1: to assess impacts of megacities and large air-pollution hotspots on local, regional, and global air quality

2: to quantify feedbacks among megacity air quality, local and regional climate, global climate change

3: to develop improved integrated tools for prediction of air pollution in megacities
Case Study 2: Paris - MEGAPOLI Project

- ATOFMS deployed at the LHVP urban background site
LHVP Site Paris

ATOFMS Sampling carried out at LHVP site, for four weeks Jan-Feb 2010
Data Analysis

- Over 1,500,000 ATOFMS mass spectra collected for Paris

- Clustering resulted in the identification of particle classes predominantly associated with fossil fuel and wood combustion

- Much more complex than Cork City; carbonaceous particles exhibited 10 distinct mixing states

*Healy et al., Atmos. Chem. Phys. 2012*
Biomass burning and fossil fuel spectra - Paris
Quantitative Approach

- While mixing state information is useful- can we achieve quantitative results with the ATOFMS?

- Obstacles include size-dependent transmission efficiency issues and composition-dependent matrix effects

- Concurrent measurements with a scanning mobility particle sizer enabled the conversion of ATOFMS particle counts to estimated mass concentrations (µg m⁻³)

- Comparison of ATOFMS mass spectral marker ions for EC, OA, and inorganic ions with independent measurements used to determine relative sensivity factors for each species
Quantitative Approach

Box-plot of hourly size-dependent scaling factors for the entire measurement period (n = 624).
Scaled size resolved number concentrations were used to generate mass concentrations for each single particle class.

The summed concentrations of the 10 classes agreed well with total PM$_1$ mass concentrations from HR-ToF-AMS/PILS/Sunset OCEC instruments.
Quantitative Results

Comparison of ATOFMS mass spectral data with concurrent HR-ToF-AMS, PILS and OCEC datasets enabled estimation of the chemical composition of each particle class.
Quantitative Results

ATOFMS data are size-resolved: enables determination of size-resolved PM$_1$ composition
Local vs regional contributions to PM$_1$

The chemical composition of PM$_1$ in Paris is highly variable and dependent upon air mass origin.
The chemical composition of PM$_1$ in Paris is highly variable and dependent upon air mass origin.
ATOFMS particle classes assigned as local or regional based on mixing state, then local and regional contributions to each species and to PM$_1$ can be estimated.

Local contributions are relatively minor, highlighting the impact of regional pollution.
Potential source regions

- Sulphate-rich particles associated with Northeastern and Eastern Europe
Summary

- Single particle mass spectrometers such as the ATOFMS enable the association of unique particles with specific sources

- Size resolved mixing state information can be used to successfully separate particles arising from traffic, domestic combustion and shipping in urban environments

- Air quality in Cork Harbour is dominated by fresh local emissions, while in Paris particles emitted outside the city can impact significantly upon local air quality

- Local contributions to PM$_1$ in Paris are estimated to be minor using ATOFMS quantitative data, a conclusion consistent with recent source apportionment studies in Paris involving multiple sites*

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Solid fuel mass spectra Cork Harbour

Coal

Peat

Wood
Uptake of nitrate - Cork Harbour

[Graph showing ATOMFS counts and wind speed over dates]
Scaling assumptions - Paris

Particle density = 1.5 g cm\(^{-3}\) for all particles (from AMS and MAAP data)

Particles are all spherical

All particles are detected with equal efficiency by ATOFMS
Quantification Paris (1)
Quantification Paris (2)
ATOFMS vs HR-ToF-AMS Paris

- ATOFMS OA (EC_{bb} + OC_{bb}) vs AMS BBOA
  - y = 0.63x + 0.16
  - R² = 0.56

- ATOFMS OA (OC_{bb} NO_{x}) vs AMS HOA
  - y = 0.40x + 0.21
  - R² = 0.67

- ATOFMS OA (EC_{ff} + ECSO_{x}) vs AMS HOA
  - y = 1.17x - 0.39
  - R² = 0.47

- ATOFMS OA (OC_{bb}SO_{x} + OC_{bb}NO_{x} + OC_{bb}SO_{x} + OC_{bb}TMA + EC_{bb}NO_{x}) vs AMS HOA
  - y = 1.47x - 0.09
  - R² = 0.81
ATOFMS vs HR-ToF-AMS size distributions