Introduction

Metals present in the atmosphere are of both natural and anthropogenic sources. The natural sources include: volcanic activity, wind blown dust, marine spray, forest fires and rock erosion and weathering. Anthropogenic sources of metals include: combustion of hydrocarbon fossil fuels, traffic emissions, power generation and industrial processes. Some metals present in the atmosphere, mainly as components of Particulate Matter (PM), are known to have adverse effects on human health, often due to their high bio-reactivity and capacity to induce oxidative stress on cells.

In order to detect metals present in aerosols ATOFMS and PIXE measurements were carried out during the "SAPUSS" measurement campaign in Barcelona in 2010. The PIXE data was used to validate the metal ion intensity temporal trends produced by the ATOFMS. The dual ion mass spectra measured by the ATOFMS provide information on the mixing state of the metal-containing particles and can thus facilitate identification of the particle sources. Using the recognised ATOFMS signals associated with specific emissions a range of different particle sources can be identified. These sources include biomass burning, wind-blown dust, sea spray, vehicular traffic and industrial emissions. Several transported events were also identified using air mass back trajectories, including a contribution from wind-blown dust originating in North Africa.

Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS)

An ATOFMS was deployed at an urban background site in Barcelona, Spain for the measurement of single particle composition in September/October 2010 as part of the SAPUSS measurement campaign. The ATOFMS measures the size and chemical composition of single particles in the size range 100-3000 nm. The instrument uses 2 sizing lasers to measure aerodynamic diameter, desorption/ionisation laser to ionise particle-bound species, and 2 collinear time-of-flight mass spectrometers to detect the resulting positive and negative ions.

Particle Induced X-ray Emission (PIXE)

Simultaneous to ATOFMS measurements, collections of particulate matter, smaller than 2.5 micrometres in aerodynamic diameter (PM$_{2.5}$), were carried out using a continuous Streaker sampler operating with a temporal resolution of 1 hour. These samples were subsequently analysed using PIXE to provide quantitative elemental composition. PIXE analyses were carried out at the 3 keV tandem accelerator of the LABEC laboratory, with a collimated proton beam whose size corresponds to one hour of aerosol sampling.

Results

ATOFS mass spectra show that iron is mainly present in two particle types: one crustal and one appearing to originate from industrial processes. Both manganese and lead exhibit good correlations between PIXE and ATOFMS during higher concentration events. These two elements both occur with a similar temporality and the peaks in both elements belong to the same particle class, and are internally mixed. The presence of vanadium measured via PIXE analysis and the ATOFMS method seem to show better agreement during periods of increased concentration. Further investigation shows that the source of vanadium is from the combustion of heavy fuel oil such as that used in shipping.

Conclusion

From the data it is seen that the ATOFMS and PIXE data both correlate when there are periods of increased concentration, however, during other periods the correlation is not as strong. This could be caused for a number of reasons including, ion interference in the ATOFMS signal and issues with the detection limit of the different elements in PIXE analysis, which could also contribute to the observations. It was also found that the ATOFMS is very useful in determining the mixing state of the different elements present along with the metals.

Future Work

In order to improve the comparison between the ATOFMS ion signal measurements and the PIXE mass concentrations the querying method for the ATOFMS data will be refined in order to remove any interferences present in the data due to the presence of ions with similar m/z. Meteorological data will be combined with the PIXE data in order to identify possible sources of metals in the atmosphere in Barcelona. PMF analysis will be used in order to identify the sources of the emissions seen.

Acknowledgements

The authors wish to thank the following: ICREA Embark Initiative The Higher Education Authority (HEA) EPA Ireland

References