

## **Aerosol source apportionment in Cork Harbour, Ireland, based on continuous, real-time measurements, Aerosol Time of Flight Mass Spectrometry and factor analysis.**

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Cork Harbour is home to Ireland's second largest port and several chemical industries. This study presents a source apportionment model for Cork Harbour developed on four levels, with the objective of quantifying the contribution of shipping emissions to local air pollution. Air quality data and samples of atmospheric aerosols were collected near the main container berth, close to the shipping channel and about 3 km from the centre of Cork City. The data includes a three month record of real-time measurements of gases  $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{O}_3$ , particulate sulfate and particulate elemental and organic carbon (ECOC) and ambient levels of  $\text{PM}_{2.5}$ , acquired in the summer of 2008. During the same period, PM collections were made continuously using a High-Volume Cascade Impactor, sampling at 900 litres of air per minute (lpm) and capturing PM on polyurethane foam (PUF) substrate in two size fractions,  $\text{PM}_{10-2.5}$  and  $\text{PM}_{2.5-0.1}$ . Two samples were obtained per week. The  $\text{PM}_{2.5-0.1}$  size fraction was analysed for inorganic ions and metals using ion chromatography and inductively coupled plasma – optical emission spectroscopy. The campaign also included collection of  $\text{PM}_{2.5}$  on quartz fibre filters over 24 hour periods for one month, using a Digital DHA-80 high volume sampler collecting 500 lpm, which were subsequently analysed for the presence of organic molecular markers by GC-MS. Finally, over a three week overlapping period an Aerosol Time of Flight Mass Spectrometer (TSI-ATOFMS) was used to characterise chemical composition of several hundred thousand individual particles, which were subsequently clustered into some 30 particle types by a K-means clustering algorithm.

The source apportionment model was developed in stages by initially subjecting each data set to factor analysis by principal component analysis and positive matrix factorisation (PMF) to resolve the main likely sources. This approach combines several independent methods and analytical protocols and allows for robust conclusions regarding likely sources to be made, because each collection method is optimised to the subsequent analysis.

The real-time record can be resolved into four main likely contributors, i.e. traffic, coal/biomass burning, regional/aged traffic emissions and a small shipping contribution to carbonaceous aerosol and sulfate. The organic content of  $\text{PM}_{2.5}$  collected in daily samples could be attributed to 3 separate sources, one of which coincided with the biomass

burning factor and 2 further biogenic factors, which were identified as fungal spores and secondary organic aerosols from biogenic emissions of sVOC.

Likewise, sources of inorganic ions and metals were resolved by a PMF model based on 3 and 4 day collection periods. These include traffic, sea salt, crustal materials and secondary inorganic aerosols. Finally, a model based on the temporal record of individual particle types identified by ATOFMS was able to both resolve factors that coincided with the other models (e.g. fungal spores, biomass burning, sea salt and crustal materials) as well as identifying sources not resolved by the other data. The temporal trends of the latter were highly correlated to the real-time measurements and chemical content of the PM collections. The final factor profiles include ions, metals, organic markers and particle types identified by ATOFMS.

The particle types identified by ATOFMS include clusters that were unequivocally identified with ship plumes, by a combination of size, chemical composition, concurrence with ship times as of schedule provided by the Port of Cork and as identified by peak events in the  $\text{NO}_x$ ,  $\text{SO}_2$  and EC records. Real-time, continuous measurements and collections of PM on PUF for determination of inorganic ions and metals have been made for a period exceeding one calendar year. The shipping particle types identified this campaign are used to "calibrate" a shipping emissions factor profile in terms of ions, metals and organic markers and allows for an estimate of the contribution of shipping over the course of the entire record available for the inorganic and organic contents.

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