Composition and Source Identification of Ambient Single Particles during the NANO-INDUS 2012 Campaign in Dunkirk, France

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Situated on the north coast of France, Dunkirk's air quality is subject not only to the high volume of shipping traffic passing through the Dover Strait, but also to the emissions from a considerable industrial sector. The city is host to the largest steel manufacturing plant in France, an oil refinery and an industrial facility with the largest manganese ferroalloy furnace (Fe-Mn furnace) in the world.

The aim of the NANO-INDUS campaign was to characterise the transient emissions from this facility. To this end a suite of online instruments and offline techniques were located approximately 1 km to the southwest of the alloy manufacturing plant, from 15th May – 10th June 2012. An aerosol time-of-flight mass spectrometer (ATOFMS, TSI model 3800), was used to determine the chemical composition and size of individual ambient particles in the vicinity of the Fe-Mn furnace in real time.

Over 700,000 single particle mass spectra were generated and then classified using the *K*-means algorithm. Based on their mixing state, size distributions and temporality, 18 major particle types were identified including: shipping, sea salt, several elemental and organic carbon types, along with some sulfur, calcium, and various Fe-containing types emitted from nearby industrial sources.

Particles containing internally mixed potassium and chloride, typically associated with biomass burning (specifically from domestic wood combustion) were found instead to be industrial in origin. This was supported by the absence of biomass burning organic aerosol (BBOA) in the co-located Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) dataset. The latter instrument was used to identify a number of sources of organic aerosol (OA) and comparison of these OA factors with the ATOFMS data has provided valuable information on the mixing state of organic aerosol in Dunkirk.

A calcium-containing particle type, usually associated with vehicular traffic emissions in urban field studies, was also found to be industrial in origin. Mass spectra for these particles were dominated by calcium (*m/z* 40, $[Ca]^+$) and carbonate (*m/z* -60, $[CO_3]^-$) and displayed a strong northeasterly wind dependence, the direction of the Fe-Mn furnace. Calcium carbonate is used as an additive in the sintering process and it is thus likely that these particles are emitted from one of the main stacks of the plant.

Fe and Mn particle types, originating from the Fe-Mn furnace were also identified. These included two Fe-containing types, one internally mixed with Na and K, the other internally mixed with Mn (Figure 1). Further Mn-containing particle types were identified and found to contain Pb and K, but not Fe. Zn-containing particles were also observed, with and without Pb. Thus, single particle mixing state was observed to be highly heterogeneous in the vicinity of the industrial facility.

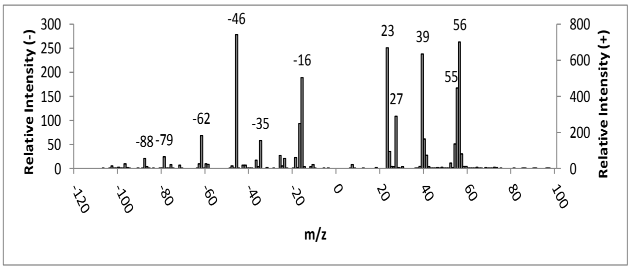

Figure 1. Average mass spectrum of Fe-Mn particles observed in the vicinity of an industrial plant in Dunkirk.

Further information on these metal-containing particles has been obtained by quantitative analysis of filter extracts using ICP-AES and ICP-MS, as well as measurements of single particles using SEM/EDX. The use of these techniques in combination with the mixing state information and high temporal resolution of the ATOFMS provides valuable insights into the sources, composition, variability and chemical processing of single particles from industrial emissions.

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