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Chemical tracers of shipping emissions in a Mediterranean harbour

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Particle emissions from transport-related activities are known as one of the most important sources contributing to the PM mass concentrations in urban environments. However, only limited information is currently available in the literature on the contribution to PM levels by specific transport related sources such as shipping emissions, even though according to the latest IPCC report (Ribeiro et al., 2007), shipping emissions are receiving increased scrutiny by international and regional regulatory agencies because of their potential impact on air quality and human health in communities downwind from major shipping lanes and ports (Dominguez et al., 2008). One of the main reasons for this lack of information is the complexity in the detection of shipping emissions, given that no specific emission tracers have so far been identified as a consequence of the vast variability of combustion fuels burnt by vessels.

The city of Melilla was selected for the study of shipping emissions due to its location on the South-Western sector of the Mediterranean basin, on the Northern coast of Morocco and less than 200 km from the Gibraltar Strait (35º17´40N̈, 2º56´30Ẅ). The city covers an extension of 13.4 km2, with a population of 70000 inhabitants. The monitoring station selected for the present study is representative of urban background levels, and it is located at approximately 150 m from the Melilla harbour. The harbour is mainly characterised by commercial traffic (passanger and container), although minerals and other loose materials are also stocked on the docks located farthest away from the monitoring site.

PM10, PM2.5 and PM1 levels were determined on an hourly basis between 12/01/2008 and 19/12/2008 using a GRIMM laser spectrometer, which produced more than 8000 data points for each size fraction (24000 data points in total). In addition, PM10 and PM2.5 levels were sampled on quartz fibre filter substrates (Munktell) by means of high-volume samplers (PM1025 MCV, 30 m3/h) at a rate of 2 samples per week for each size fraction. This resulted in 78 and 77 valid PM10 and PM2.5 samples, respectively. All samples were weighed and analysed for major and trace elements following the methodology described by Querol et al. (2004).

The data collected over the annual period was analysed as a function of the wind sectors defining the main PM sources: 0-45º (open sea), 45-135º (harbour) and 135-360º (land). PM levels and chemical composition were evaluated for each of these sectors, and initial results on hourly PM levels (24000 data points) showed striking similarities between the results from the open sea (46 μgPM10/m3, 22 μgPM2.5/m3, 14 μgPM1/m3) and the harbour (44 μgPM10/m3, 21 μgPM2.5/m3, 13 μgPM1/m3) sectors, which were markedly different from those recorded from the land (37 μgPM10/m3, 16 μgPM2.5/m3, 11 μgPM1/m3). This indicated that the impact of shipping emissions on urban background PM levels do not represent only harbour emissions, but also emissions produced during vessel traffic into and out of the harbour, and also across from Melilla and through the Gibraltar Strait. The same kind of analysis was carried out for the levels of tracers species and tracer ratios, in search for a marker of shipping emissions. Results showed that the V/Ni ratio followed a similar pattern to that detected for PM levels, with similar values for the open sea and harbour sectors (4.1 and 4.0, respectively), which differed widely from the ratio obtained from land (12.4). These results evidence the value of the V/Ni ratio as a marker for shipping emissions in Melilla.

Further research is ongoing in search of other tracer species and/or tracer ratios. Furthermore, a source apportionment analysis will be carried our by means of PMF, which will be followed by a Multi-linear Engine (ME)

analysis with pulling towards the marker V/Ni ratio and aimed at quantifying the impact on urban PM levels of shipping emissions in Melilla.

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