## Source apportionment of ultrafine and fine particles in Huelva industrial city

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Urban air quality impairment by ultrafine particles (diameter  $< 0.1 \ \mu m$ ) has become a matter of concern due to the adverse effects on human health (Araujo and Nel, 2009). Most of the studies of ultrafine particles in urban air quality have focused on vehicle exhaust emissions. Thus, ultrafine particle emissions in vehicle exhaust have been subject to limit values in a recent stage of the EURO standards.

We present a study on how industrial emissions contribute to ultrafine particle concentrations in downwind urban ambient air. This research is based on experimental data collected in the ambient air of the industrial city of Huelva (SW Spain) over 18 months (particle number concentration, black carbon and levels and composition of PM<sub>2.5</sub> with daily resolution). This city is affected by emissions from the second largest Cusmelter in Europe, phosphoric acid and fertilizer production plants and an oil refinery and petrochemical plant. In order to quantify the process contributing to ultrafine particles concentrations (N), two components (N1 and N2) were segregated by the methodology of Rodríguez and Cuevas (2007). N1 accounts for vehicle exhaust emissions and may also include compounds nucleating/condensing immediately after emission. N2 is correlated with SO<sub>2</sub> and accounts for new particle formation due to nucleation and rapid particle growth to detectable sizes (Fernández-Camacho et al., 2010b).

In order to identify the sources contributing ultrafine particles, Principal Component Analysis were performed to data for particle number concentration and  $PM_{2.5}$ chemical composition. Three Principal Components were observed: APC-1, showing a high association with species linked to industrial emissions from the Cu-smelter (nss-SO<sub>4</sub><sup>-</sup>, As, Sb, Pb, Zn and Sn), the phosphoric acid and fertilizer plant ( $nss-SO_4^{=}$ , P and  $NH_4^+$ ) and the oil refinery (nss-SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, V and Ni). The presence of N2 in this PC is attributed to ultrafine sulphate particle formation in the plume during inland transport prompted by sea breeze from 09:00 to 17:00 GMT (Fernández-Camacho et al., 2010b); APC-2 associated with road traffic emissions: vehicle exhaust emissions (OM and N1) plus road dust (Al, Ca, Fe, Ti, Mn and K). The presence of N1 in this factor is in agreement with the weekly cycles of NO<sub>x</sub> and N1 particles, which exhibits high values during working-day rush hours (view details in Fernández-Camacho et al. 2010b); APC-3 showing high factor loading for typical sea salt components (Cl, Na and Mg). As expected,

neither of the particle number components, N1 or N2, was associated with this factor.

Only two sources contributed significantly to the particle number N: road traffic accounted for  $50 \pm 9\%$ , whereas industrial emissions accounted for  $44 \pm 7\%$  of N. Figure 10 shows the daily mean averaged values of the particle number N, classified from the highest to the lowest concentration  $(100^{\text{th}} \text{ to } 1^{\text{st}} \text{ percentile})$ , and the contribution of the identified sources. When vehicle exhaust is the main source, ultrafine particles typically show (24-h mean) concentrations within the range 14700 – 5000 cm<sup>-3</sup> ( $50^{\text{th}} - 1^{\text{st}}$ ), with 60% of these being linked to this source and 30% to industrial emissions. In contrast, when daily mean levels of N are within the range 50000 – 25500 cm<sup>-3</sup> ( $100^{\text{th}} - 70^{\text{th}}$ ) industrial and vehicle exhaust emissions accounted for 49 and 30%, respectively.

The results of this study show that industrial emissions are the main cause of ultrafine particles episodes in Huelva city.



Figure 1. Daily averaged values of N classified from highest to lowest concentration highlighting the contribution of the industrial, vehicle exhaust and undetermined fraction contributions.

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