

# Size distributed metallic elements in submicron and ultrafine atmospheric particles from urban and industrial areas: a source assessment

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In recent decades, studies have evidenced the relationship between high concentrations of airborne particles (PM) and increased mortality and morbidity related to respiratory and cardiovascular diseases (Künzli *et al.*, 2000; Pope et Dockery, 2006). PM<sub>10</sub> and PM<sub>2.5</sub> are usually selected as the monitoring parameters for air quality evaluations. However metallic elements associated with inhalable particles, particularly in the finest fraction, have been shown to increase human lung and cardiopulmonary injuries (Schaumann *et al.*, 2004; Osornio-Vargaset *et al.*, 2003). In toxicology and source assessment, particle size is a key parameter. The objective of the present study is to give new insights about the size distribution and source emissions of potentially toxic heavy metals in an urbano-industrial area representative of other major industrial regions in Europe.

The PM<sub>10</sub>, PM<sub>1</sub> and PM<sub>ultrafine</sub> fractions were collected under “industrial” and “urban-traffic” wind sectors, in one of the largest industrial cities of France (Dunkirk) during winter 2012. The PM were sampled using low pressure cascade impactors and elemental analyses were performed by ICP-AES (Al, Ca, Fe, K, Mg and Na) and ICP-MS (As, Ba, Cd, Co, Cr, Cu, La, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Ti, V and Zn).

Both, meteorological conditions and emission sources variability were found to be important parameters that control the size distribution and the chemical composition of particles. The PM<sub>10</sub>, PM<sub>1</sub> and PM<sub>0.29</sub> mass concentrations were respectively  $23.6 \pm 6.0$ ,  $10.1 \pm 4.1$  and  $2.4 \pm 1.1$   $\mu\text{g}/\text{m}^3$ , under industrial influence and  $29.8 \pm 4.1$ ,  $16.6 \pm 3.9$  and  $5.8 \pm 2.1$   $\mu\text{g}/\text{m}^3$  under urban-traffic influence. Regarding the relative concentration of the twenty three elements investigated, the submicron fractions (PM<sub>1</sub> and PM<sub>0.29</sub>) accounted respectively for about  $41.8 \pm 10.8\%$  and  $9.8 \pm 2.4\%$  of the PM<sub>10</sub> mass for the industrial sector and  $56.8 \pm 16.2\%$  and  $20.2 \pm 9.3\%$  for the urban-traffic one. This comparison suggests that urban sources produce, in average, finer particles and in a larger amount than industrial sources. Regarding the relative concentration of metallic elements, the submicron fractions (PM<sub>1</sub>) represented  $46 \pm 24\%$  for industrial and  $52 \pm 23\%$  for urban-traffic sectors, with

generally higher proportions for the ultrafine fraction (PM<sub>0.29</sub>) under an urban-traffic sector influence ( $14 \pm 8\%$  and  $24 \pm 9\%$ , respectively), associated to sources located within the city and suburban traffic.

This result imply that, even for an urban environment potentially influenced by the proximity of metallurgical activities, traffic within the urban district and nearby house heating may overwhelmingly influence the metallic content of atmospheric nanoparticles. However, industrial processes may significantly affect the neighboring urban atmosphere with metal-rich particles, especially in the accumulation mode (PM<sub>0.29-1</sub>). They have been attributed, in this size range, to primary particles emitted by steelworks and metal refinery processes. These aerosols can easily reach our sampling site located in the nearby urban area (2000 m). We also evidenced that vehicular emissions remain the main sources of Cu and Sb in the submicron fraction.

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