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Size-distributed metallic elements in submicronic and ultrafine atmospheric particles from urban and industrial areas in northern France

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ABSTRACT

To determine the size distribution of potentially toxic trace metals (TM) in atmospheric particulate matter (PM), sampling experiments were performed in the urban–industrial area of Dunkirk (North of France) during winter 2012. Total mass concentrations are in accordance with typical values obtained at European urban background sites but lower than the concentrations reported for some Asian industrial countries. Considering the local wind directions, mass concentrations are higher downwind of urban influences than downwind of industrial emissions. The mean PM_{10} mass concentration (25–30 μg/m^3) is less than the European Union and US EPA limit values (40–50 μg/m^3) but greater than the WHO guidelines (20 μg/m^3). The calculated TM crustal enrichment factors (EF_{Crust}) suggest the anthropogenic origins of most of the studied TM (Sb, Cd, As, Mo, Pb, Zn, Cu, Ni, Cr, Mn and V). The highest TM concentrations were obtained for Zn and Mn (>50 ng/m^3) under industrial influence, but the finest particle (< 0.29 μm) concentrations were higher for the urban sector than for the industrial sector. This enrichment may be attributed to local urban traffic. In contrast, trace metals are more abundant in the coarser fraction (> 0.29 μm) downwind of industrial emissions. Moreover, mechanical operations associated with industrial processes (excavating, crushing, and sintering), as well as the resuspension of industrial soils, likely represent some significant TM source-terms in the supermicronic fraction. The EF_{Crust} comparison between the two prevailing sectors demonstrates the importance of steelworks and smelting emissions in the abundance of some TM (As, Cd, Fe, Mn, Mo, Pb, Rb and Zn). In contrast, the Cr and Co concentrations seem to be more related to coal combustion emissions, Cu and Sb to automotive traffic, and V, La and Ni to petrochemical activities.

1. Introduction

Over the past several decades, atmospheric particulate pollution and its related human health impacts have become a major concern not only for researchers but also for governments and the general public, particularly in urban and highly industrialized areas (Chapman et al., 1997; Dockery et al., 1993; Pope-III and Dockery, 2006). Airborne particulate matter (PM) comes from natural and/or anthropogenic sources through various physicochemical processes (Buseck and Adachi, 2008; Horvath et al., 1996) that greatly influence their concentration, size distribution and chemical composition (Pakkanen et al., 2001). Primary particles are directly emitted into the atmosphere, whereas secondary PM may also occur through homogeneous or heterogeneous

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chemical transformations of particulate/gaseous pollutants (Buseck and Adachi, 2008). Among the many criteria for PM classification, the size (defined as an equivalent diameter) is one of the most important parameters. The aerodynamic diameter (D_p) is commonly used to divide PM into coarse (2.5 μm < D_p < 10 μm), fine (0.1 μm < D_p < 2.5 μm) and ultrafine (D_p < 0.1 μm) fractions. Coarse particles are generally emitted through natural and mechanical processes (soil erosion from wind, abrasion by friction, resuspension of dust from roads or storage piles, or marine aerosols). Fine ($PM_{2,5}$) and ultrafine particles ($PM_{0,1}$) originate largely from anthropogenic sources, such as combustion processes and/or photochemical reactions and gas to particle conversion (condensation and coagulation). Depending on the size of the constituent particles, PM may remain suspended for minutes to weeks in the atmosphere (Buseck and Adachi, 2008) and is removed by dry or wet deposition at various distances from the sources (Seinfeld and Pandis, 1998).

Industrial processes, such as metal refining and fossil fuel combustion, are known to release fine particles ($PM_{2,5}$ and $PM_{0.1}$), which are often very enriched in trace metals (TM) (Gao et al., 2002; Jang et al., 2007; Prati et al., 2000). In contrast with many organic compounds, most trace elements are only slightly influenced by atmospheric processes during their transport in the atmosphere and can therefore be considered conservative tracers (Zhang et al., 2011; Alleman et al., 2010; Dongarrà et al., 2009; Lim et al., 2010; Morawska and Zhang, 2002; Ny and Lee, 2011; Wu et al., 2007) of urban and industrial sources (e.g., As, Cu, Fe, Mn, Pb for steelworks and non-ferrous metallurgy; Cr for coal combustion; Ni and V for fuel and oil combustion; Cd, Pb and Zn for waste incineration; and Sb, Cu and Ba for road traffic).

Particle size governs the toxicity of the aerosols by controlling the transfer and deposition sites in the airways of the lungs (Donaldson et al., 2002). Fine particles penetrate deep into the pulmonary system and are therefore difficult to eliminate. Furthermore, submicron particles, especially $PM_{0,1}$, have a very high number concentration and specific surface area, which confer important surface chemistry in contact with the epithelial cells (Donaldson et al., 2002). Consequently, metallic elements containing $PM_{2,5}$ and $PM_{0,1}$ (bronchoalveolar fractions) are potentially more harmful when inhaled (Schaumann et al., 2004). Some of the metallic elements are highly toxic (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Hg and Pb) (Campen et al., 2001; Donaldson et al., 2002; Garçon et al., 2006) and are known as human carcinogens (Cr, As, Cd and Ni). Therefore, determining the size-resolved chemical composition of particles is crucial in quantifying their potential deleterious effects on human health and to the environment.

Most previous studies of PM and associated metallic elements have generally focused on the total suspended particles (TSP), PM_{10} and, more recently, on $PM_{2.5}$. These studies often analyzed urban PM (Cabada et al., 2004; Fang et al., 2000; Rizzio et al., 1999), and there have been very few studies investigating the size distribution of metallic elements in industrial areas (Hieu and Lee, 2010; Ny and Lee, 2011; Oravisjarvi et al., 2003; Prati et al., 2000), particularly for the submicron fractions (PM_1).

Approximately 30% of PM_{10} emissions in France (CITEPA, 2011) are due to industrial activities. The Dunkirk region is one of the most industrialized zones in France and the third largest French commercial harbor. Some previous studies performed in this region (Alleman et al., 2010; Garçon et al., 2006; Ledoux et al., 2006) indicated that the air quality in Dunkirk was clearly affected by emissions from the harbor industrial complex and heavy diesel motor vehicles. However, these studies did not specifically consider the fine and ultrafine fractions and did not assess their most common sources.

The goal of the present study is to provide insights regarding the size distribution of potentially toxic heavy metals (from PM_{10} to ultrafine particles) in an urban–industrial area, representative of major industrial regions in Europe. We performed a tentative source assessment based on these findings and compared it with previous studies.

2. Material and methods

2.1. Sampling location

The sampling site, previously described in Alleman et al. (2010), is represented in Fig. 1. Briefly, it is located in the Dunkirk region (210 000 inhabitants), a French harbor along the southern bight of the North Sea. The Dunkirk area is connected by highways with high traffic density (A25: ≈40 000 vehicles/day; A16: ≈30 000 vehicles/day). The local climate is characterized by humid (120 days of rain per year) and cool temperatures, with monthly means ranging from 5 to 16 °C, inducing a rather long heating season (October to May). The region is characterized by the use of natural gas heating (65% of the heating energy), whereas coal, oil and wood for home heating are less common in the Dunkirk area (10%). The sampling station was situated on the roof of an elementary school (≈6 m high), in the suburb of Grande-Synthe City, approximately 2 km south of the main industrial complex, which includes steel, cement and petrochemical plants, refineries, and port activities. The industrial area is also under the influence of the seashore, which regularly brings fresh air masses towards the land and the sampling site.

2.2. Particle collection

We collected PM in January and February 2012 using the cascade impaction technique to separate atmospheric particles depending on their aerodynamic diameter through impaction plates, with each corresponding to a specific cut-off diameter. For this purpose, collection was performed in parallel with 3-stages (50% efficiency equivalent aerodynamic diameters – $D_{p,50}$ – respectively equal to 10, 1 and 0.1 μm, plus a backup filter) and 13-stages of cascade impactors (DEKATI™) ($D_{p,50}$ respectively equal to 10, 6.7, 4.0, 2.5, 1.65, 1.0, 0.65, 0.4, 0.25, 0.17, 0.1, 0.06 and 0.03 μm), operating at a flow rate of 30 l/min on polycarbonate membranes (25 mm diameter, Whatman™). The two impactor types were used (1) to obtain a detailed segregation of the particle sizes (provided by the 13-stage impactor) and (2) to collect a sufficient mass for trace element analyses (with the 3-stage impactor). The PM_{10} and PM_1 fractions were determined by summing the masses collected on the impaction stages (filter substrates) with $Dp_{,50}$ < 10 and 1 μm,