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Metal-bearing fine particle sources in a coastal industrialized environment

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ABSTRACT

Fine (<2.5 μm), submicron (<1 μm) and ultrafine (<100 nm) atmospheric particles were collected during a 3-weeks campaign in a heavily industrialized area and physically and chemically characterized in order to determine their main sources. As a basis of comparison, the present one-year average EU limit value (25 $\mu g \cdot m^{-3}$) and the WHO recommendation for $PM_{2.5}$ (10 $\mu g\ m^{-3}$) were regularly exceeded during this campaign. Submicron particles (PM_1) account for 55 to 70% of $PM_{2.5}$ mass concentrations. A bi-modal size distribution, centered on 0.4 and 2.0 μm, suggests two types of emissions: high temperature processes that liberate primary or secondary submicron particles and mechanical procedures in open air, or local traffic, which lead to the emission of coarser particles (>1 μm). The trace elements As, Cd, Ni, Pb, Sb, V and Zn, characteristics of the local industrial activities display 60% to 85% of their mass in the submicron and ultrafine fractions and appear highly enriched, by reference to the crustal source. High atmospheric pressure periods, corresponding to northeasterly winds, induce the highest contributions of metalworking emissions and the highest $PM_{2.5}$ concentrations (32.5 ± 11.9 $\mu g \cdot m^{-3}$). A Principal Component Analysis of the dataset produces 7 factors associated to metallurgy-, steelworks-, oil processing-, coal combustion-, neighboring traffic-, dust resuspension- and sea salt-sources, that explain the obtained concentrations. A Multiple Linear Regression Analysis confirms that Fe-Mn alloy refining, iron- and steelmaking are the main sources (>40%) controlling metal concentrations in $PM_{2.5}$. Less predictably, resuspended dust and fresh/aged sea salts are also significant contributors (≈20%). Considering the related health hazards, authorities should pay more attention to the exposure of people living in this area and the possible impact of fine particles in terms of public health.

1. Introduction

Industries such as metallurgy, oil and coal combustion, petrochemistry and the cement industry are known to produce fine particles ($PM_{2.5}$, particulate matter with an aerodynamic diameter <2.5 μm) during combustion, sintering, crushing, casting or welding (Fernandez-Camacho et al., 2012). Air pollution control devices implemented in industrial facilities are usually not designed for an optimized abatement of these fine particles. Diffuse emissions are also strong contributing sources (Tolis et al., 2015). Among $PM_{2.5}$, primary combustion particles are believed to be more harmful to human health than secondary particles produced through chemical reactions that convert gaseous substances to particulate matter (Tuomisto et al., 2008). Exposure to $PM_{2.5}$ has been progressively recognized to have a strong impact on human health, increasing mortality and morbidity rates due to respiratory diseases such as asthma, chronic obstructive pulmonary disease, cancers and cardiovascular diseases (Atkinson et al., 2010; Dockery, 2001; Dockery and Pope, 1994; Pope et al., 2004). While European current regulations tend to limit fine particle concentrations in the ambient air to <20 $\mu g \cdot m^{-3}$, there are no specific standards for industrial facilities. Recent studies and reviews (Hieu and Lee, 2010; Mbengue et al., 2014; Riffault et al., 2015; Sanderson et al., 2014; Vecchi et al., 2008) have demonstrated that, for example, World Health Organization (WHO) and European Unions (EU) recommendations (1-year average limit value: 10 $\mu g \cdot m^{-3}$) are regularly exceeded in urban environments influenced by nearby industrial activities. In spite of broad emission regulations, industrial activities have a significant contribution to the global load of atmospheric particulate matter in Europe ($1.3 \times 10^6\ t \cdot yr^{-1}$ of $PM_{2.5}$, accounting for 40% of the total PM_{10} emissions), with two industrial sectors, International Energy Agency (I.E.A.) meaning, i.e. manufacturing industry and industrial processes, accounting for 15.6% of $PM_{2.5}$ (Pulles et al., 2007).

Atmospheric particles measured in industrial areas are generally enriched in potentially toxic trace metals (Fernandez-Camacho et al.,

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2012; Gao et al., 2002; Jang et al., 2007; Lim et al., 2010; Osornio-Vargas et al., 2003; Schaumann et al., 2004). Some of these metals are linked to lung inflammation and damage (Claiborn et al., 2002; Osornio-Vargas et al., 2003). They can generate Reactive Oxygen Species (ROS), inducing a cellular pro-inflammatory response (Majestic et al., 2007; Schaumann et al., 2004) and are therefore considered to play a role in chronic obstructive pulmonary disease and asthma. Most of these trace metals (As, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Rb, Sr and Zn) are only slightly influenced by atmospheric processes during their transport and can therefore be considered as conservative tracers.

Consequently, trace metals have been largely used in source-receptor modeling, to distinguish individual sources of pollutants in multi-influenced industrial and urban environments (Alleman et al., 2010; Belis et al., 2013; Manoli et al., 2002; Ny and Lee, 2011; Oravisjarvi et al., 2003; Taiwo et al., 2014; Viana et al., 2008). These studies led to chemical source profiles database as the U.S. EPA "SPECIATE" database or the recent European "SPECIEUROPE" database (Belis and Pernigotti, 2015). Especially, some $PM_{2.5}$ sources apportionment studies using Positive Matrix Factorization (PMF) have shown that coal combustion, metal processing and refining, iron and steel manufacturing, waste and sludge incineration and cement/lime production, represent major sources of fine particles (Morishita et al., 2011a, 2011b). It is thus particularly important to characterize these metal-rich fine particles and estimate their source contribution to the ambient air pollution, especially near densely urbanized areas.

The present paper proposes to identify and apportion the main industrial sources contributing to metal-bearing fine particle concentrations in one of the most important coastal industrial area in Europe. For that, $PM_{2.5}$ mass concentrations and their metal content have been measured, with an emphasis on the extent to which submicronic (PM_1) and ultrafine/nanometric ($PM_{0.1}$) fractions can be related to industrial processes or associated manufacturing operations. Finally, Principal Component Analysis (PCA) and Multiple Linear Regression Analysis (MLRA) have been used to assess the source contributions to the 23 metal concentrations measured in $PM_{2.5}$.

2. Material and methods

2.1. Site description and sampling campaign

The sampling site is located in the industrial area of Dunkirk, a French harbor (210,000 inhabitants), along the southern bight of the North Sea (Fig. 1), near the Dover Straits. Dunkirk is one of the most industrialized zones in France and the third largest French industrial harbor. The main industrial complex including metallurgical and petrochemical plants is connected by high traffic density highways (A25: ~40,000 vehicles/day; A16: ~30,000 vehicles/day). This sampling site allows us to collect metal-bearing particles from various plants located in the harbor. More particularly, the site is located in the neighborhood of two metallurgical facilities, in the northeast (Fig.1): a Fe—Mn smelter, approximately 800 m away and steelworks, 2000 m away.

The field campaign (May 15th–June 6th 2012) was carried out in quite similar meteorological conditions to those observed over year 2012 (Fig. 2 and Fig. S2 in Supplementary materials for the 2012 Wind Rose). Sampling was achieved using a 13-stages cascade impactor (DEKATI™), operating at a flow rate of 30 L/min. This sampling device is described in Mbengue et al. (2014). The sampling periods were conducted according to local wind directions, which are subject to rapid changes, due to small scale turbulences within the atmospheric boundary layer. The cascade impactor was connected to an isokinetic sampler head, operating 7 m above ground level, for 24 to 48 h sampling periods, during the whole campaign. The isokinetic particle sampler (IPS),

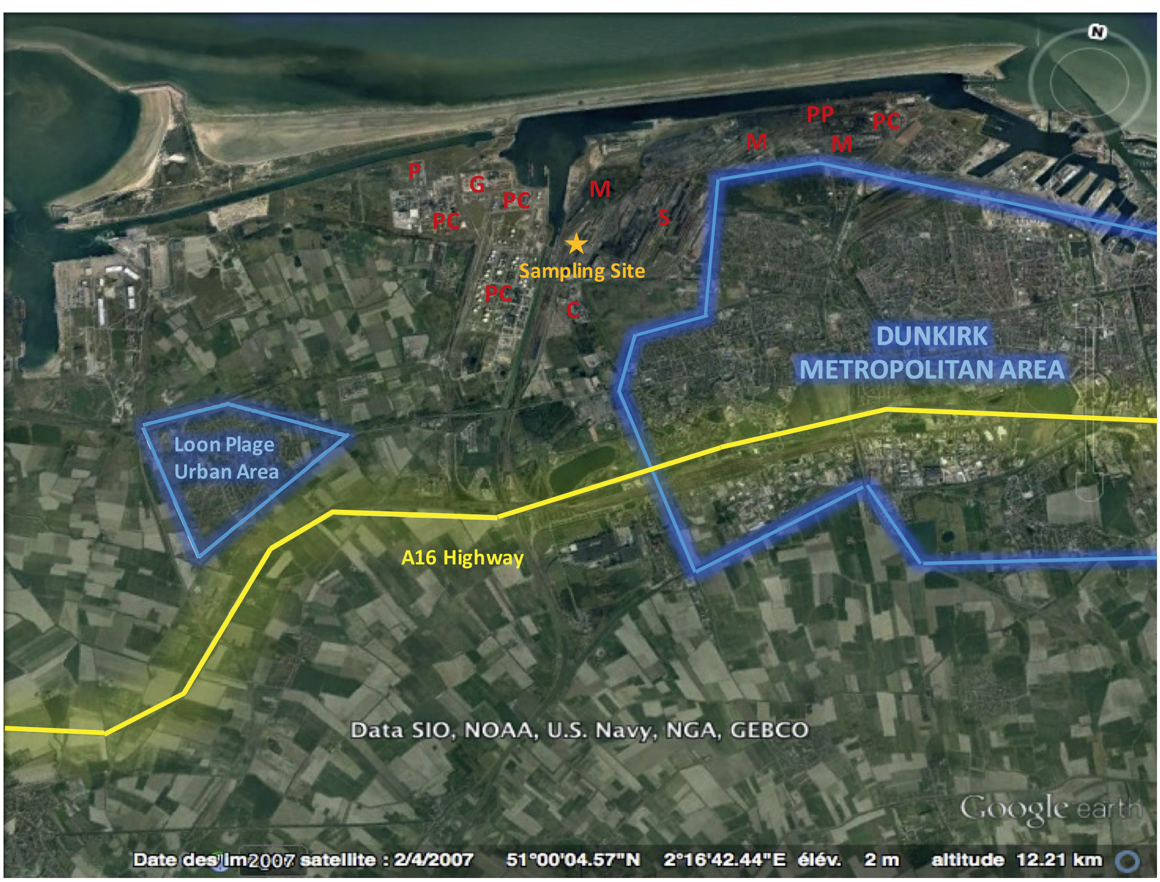

Fig. 1. Map of the industrial area near Dunkirk Harbor, with the locations of the sampling site, the main industries and Dunkirk Metropolitan area. *Key:* **C** chemical plant; **G** glass manufacturing factory; **M** metallurgy; **P** plastic manufacturing plant; **PC** petrochemicals; **PP** power plant; **S** steelworks.