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$PM_{2.5}$ source apportionment in a French urban coastal site under steelworks emission influences using constrained non-negative matrix factorization receptor model

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ABSTRACT

The constrained weighted-non-negative matrix factorization (CW-NMF) hybrid receptor model was applied to study the influence of steelmaking activities on $PM_{2.5}$ (particulate matter with equivalent aerodynamic diameter less than 2.5 μm) composition in Dunkerque, Northern France. Semi-diurnal $PM_{2.5}$ samples were collected using a high volume sampler in winter 2010 and spring 2011 and were analyzed for trace metals, water-soluble ions, and total carbon using inductively coupled plasma – atomic emission spectrometry (ICP-AES), ICP - mass spectrometry (ICP-MS), ionic chromatography and micro elemental carbon analyzer. The elemental composition shows that NO_3^-, SO_4^{2-}, NH_4^+ and total carbon are the main $PM_{2.5}$ constituents. Trace metals data were interpreted using concentration roses and both influences of integrated steelworks and electric steel plant were evidenced. The distinction between the two sources is made possible by the use Zn/Fe and Zn/Mn diagnostic ratios. Moreover Rb/Cr, Pb/Cr and Cu/Cd combination ratio are proposed to distinguish the ISW-sintering stack from the ISW-fugitive emissions. The a priori knowledge on the influencing source was introduced in the CW-NMF to guide the calculation. Eleven source profiles with various contributions were identified: 8 are characteristics of coastal urban background site profiles and 3 are related to the steelmaking activities. Between them, secondary nitrates, secondary sulfates and combustion profiles give the highest contributions and account for 93% of the $PM_{2.5}$ concentration. The steelwork facilities contribute in about 2% of the total $PM_{2.5}$ concentration and appear to be the main source of Cr, Cu, Fe, Mn, Zn.

Introduction

Suspended particulate matter constitutes a dangerous atmospheric component due to its adverse effects on human health. In this context, there is a major scientific interest to focus the attention on small size particles as $PM_{2.5}$ (particulate matter with equivalent aerodynamic diameter less than 2.5 μm), since they are able to penetrate deeply inside the lungs all the way to the pulmonary alveoli (Aphekom, 2011). The consequences of its inhalation range from an increased

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risk of asthma to cardiovascular and respiratory diseases, leading in some cases to the development of lung cancers (Perez et al., 2009; PopeIII and Dockery, 2006; Samoli et al., 2014). Consequently in 2013, the International Agency for Research on Cancer (IARC) designated PM in outdoor air as a group I carcinogen to humans (Loomis et al., 2013).

Many countries in Europe encountered difficulties while coping with the air quality guidelines of the World Health Organization (WHO) regarding daily $PM_{2.5}$ concentrations (25 μg/m^3). Recently, Salameh et al. (2015) compared the $PM_{2.5}$ concentration levels and their composition in five European cities (Barcelona, Marseille, Genoa, Venice and Thessaloniki) in the Mediterranean basin over a period of one year (2011–2012). They found that daily $PM_{2.5}$ concentrations exceeded the value of 25 μg/m^3 in several cities up to 78% and 39% of the days in Thessaloniki and Venice respectively. During pollution episodes, the composition of $PM_{2.5}$ was dominated by NO_3^- followed by SO_4^{2-} for all sites but a high contribution of mineral matter was specifically evidenced at Thessaloniki and was related to the influence of local sources. Previously, Sillanpää et al. (2006) studied the composition of $PM_{2.5}$ in European cities including Mediterranean (Barcelona, Athens), Central Europe (Prague) and North and Western Europe (Duisburg, Amsterdam, Helsinki) sites. Organic matter and secondary inorganic ions were found as the major components in $PM_{2.5}$. The differences observed in the composition of $PM_{2.5}$ from one city to another were explained in the case of organic matter by the influence of local combustion sources and the effect of domestic heating, mainly in Central and Northern Europe. The most abundant secondary inorganic ion was SO_4^{2-} at all sites, except in Amsterdam where NO_3^- was the main inorganic component. The authors also observed high NO_3^- concentration levels during wintertime periods characterized by average low temperatures.

Up to our knowledge, only few studies were conducted on the composition of atmospheric $PM_{2.5}$ in the North of France. Significant information on PM composition was proposed for PM_{10} (particulate matter with equivalent aerodynamic diameter less than 10 μm) in an urban background site over a one-year period (Waked et al., 2014). It highlighted the contribution of secondary inorganic aerosols, aged sea salts, biomass burning and primary biogenic emissions. Furthermore, scientists also focused their attention on the air quality in Dunkerque, an industrialized site located on the North-Sea coast (Alleman et al., 2010; Ledoux et al., 2002, 2004, 2006; Rimetz-Planchon et al., 2008) and where different industrial facilities, such as integrated steel plant, metallurgy, oil refinery, cement plant and hydrocarbons cracking are identified as particles emitters (E-PRTR, 2012). In this study area, industrial sources were shown to affect PM and metal (Fe, Ca, Mg, K, Zn, Mn, Pb, Cd, Cr, …) concentrations.

Many receptor and dispersion models are still being used in different countries for source apportionment studies. An assessment on the European use of modeling techniques was reported in a review on the source apportionment studies conducted in European countries (Frangkou et al., 2011). The review concluded with a list of improvements to be considered in future similar studies, such as the inclusion of uncertainty data in the input and the output, the search for specific source tracers, the use of large data matrices or increase the time coverage of the measurement campaigns, and work on solving the difficulty of separating chemically close PM (like mineral dust and re-suspended traffic dust). Most recommendations pushed in the direction of the use of hybrid models which consider a priori knowledge on the sources of emissions in order to overcome this last challenge as concluded in an important review on the methods and results of different source apportionment techniques used in Europe (Viana et al., 2008). In addition, this latter came out with a crucial list of important recommendations to fill the gaps with the currently used models. Between these recommendations we cite the use of uncertainties, the search for natural source contributions, the identification of biomass combustion sources, the separation between regional “secondary sulfate” and “secondary nitrate” profiles, and the use of hybrid models. In the scope of this study, the use of a constrained receptor model appears of particular interest in the attempt to separate sources characterized by similar elements in their chemical profiles, as the industrial profiles related to integrated steelworks emissions (Hleis et al., 2013; Machemer, 2004; Taiwo et al., 2014).

The present work aims at the determination of the chemical composition of $PM_{2.5}$ in Dunkerque and provides a source apportionment study by the application of a constrained weighted non negative matrix factorization model (CW-NMF). The first objective of the study is to evidence the influence of industrial emissions on metal concentration following the interpretation of concentration roses by wind sector and propose relevant concentration ratios permitting the identification of industrial emitters. The second objective is to identify $PM_{2.5}$ sources and quantify their contributions. Our approach was to deduce from the characteristics of metal concentrations under industrial influences the a priori information that can be considered in the NMF model calculation.

1. Materials and methods

1.1. Sampling site

$PM_{2.5}$ samples were collected at Dunkerque, northern France, a heavy industrialized city counting about 200,000 inhabitants with its suburbs and located in the southern coast of the North-Sea (Fig. 1). The sampling site was placed in the city center (latitude: 51°2′10″N; longitude: 2°22′46″E) in order to seize the urban and industrial emissions. Hence, depending on wind directions, the site can be subjected to various influences, *i.e.*, urban activities including traffic emission mainly within the 60–290° wind sector, industrial activities (metallurgy, oil refineries, cement plant, organic chemistry, *etc.*) from the industrial park implanted in the western side of the city and between them we can underline the presence of an important integrated steel works (ISW) factory producing about 6000 ktons of steel per year and covering 7 km^2 (260–290° wind sector); at the East of Dunkerque city, the presence of an electric steel plant (ESP) with a production capacity of 350 ktons of special steel in Leffrinckouke (30–90° wind sector) should be noted.

According to the European pollutant release and transfer register (E-PRTR), the integrated steelworks (ISW) and the electric steel plant (ESP) emitted 2658 tons and less than 100 tons of total suspended particles in 2010 respectively.