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.

Keywords:
PM$_{2.5}$, Receptor modeling, Non-negative matrix factorization, Source apportionment, Steelworks

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...
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 (ARC) 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 (Allenman et al., 2010; Ledoux et al., 2002, 2004, 2006; Rimetz-Planchnon 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.
More precisely, several metals were released in the air by the two factories. On a yearly average in 2010 and in decreasing order of mass, the ISW emitted Pb (6100 kg) > Zn (2180 kg) > Cu (1130 kg) > Cr (593 kg) > Ni (83 kg) whereas the ESP emissions were dominated by Zn (4190 kg) > Cr (313 kg) > Pb (227 kg) > Ni (177 kg) > Cu (111 kg).

1.2. Sampling methodology

Atmospheric particles were sampled continuously during two seasonal campaigns using the automated high volume DA80 (DA80, DIGITEL®, Switzerland) sampler equipped with a PM$_{2.5}$ cut-off diameter impactor head working under 30 m$^3$/hr air flow rate at 15°C, 1013 hPa. The first campaign covered the autumn-winter period (from 16th November to 31st December, 2010) and the second one was achieved in spring (10th March to 30th April, 2011). Semi diurnal sampling strategy was adopted to cover the 00:00–12:00 UTC and 12:00–24:00 UTC time period. The sampler was loaded with 150 mm diameter composite filters formed by two main matrices: cellulose filters (grade 41, Whatman®, GE Healthcare Life Sciences, United Kingdom) and high purity quartz microfiber filters (grade QM-A, Whatman®, GE Healthcare Life Sciences, United Kingdom). The first type is used for metal and ion analysis, and the second for carbon quantification. The cellulose filters were washed by a mixture of acids and ultrapure water (Ledoux et al., 2006), whereas the quartz filters were heated up to 450°C in a closed aluminum foil pouches for 12 hr in order to decrease their carbon content to below detection limit. Filters were retrieved from the sampler every 7 days. After sampling, all filters were released from the holder, placed under a laminar flow hood and stored in a freezer (−20°C) prior to analysis. Finally, meteorological and PM$_{2.5}$ concentration data were retrieved from Météo-France and Atmo Nord-Pas-de-Calais air quality monitoring network, respectively.

1.3. Analysis

1.3.1. Metals

For elemental analysis, samples were digested by a mixture of acids according to the method detailed in Ledoux et al. (2006). Briefly, approximately 1/8th of each cellulose filter was cut and placed into a polytetrafluoroethylene (PTFE) flask, then digested with 5.5 mL of HNO$_3$/HF/HClO$_4$ (4/1/0.5 V/V/V, Suprapur® grade, Merck®, Darmstadt) at 120°C for 4 hr. The acids were then evaporated at 170°C for 2 hr and ultrapure water was added to the residue and kept at 50°C for 1 hr. Finally, the cooled solution was diluted with ultrapure water (MilliQ®, 18.2 MΩ cm, Millipore, United States of America) up to 13 mL added with 0.2% of nitric acid and filtered on PTFE membrane (0.45 μm, VWR, USA) prior to analysis. The obtained solution was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, iCAP 6000 Series, Thermo Scientific, UK), to quantify Al, Ba, Ca, Fe, K, Mg, Na, Sr, Zn. In addition, ICP-mass spectrometry (ICP-MS, Varian® 820-MS, Varian, USA) equipped with a collision reaction interface (CRI) without or using helium as collision gas to minimize polyatomic interferences was used to quantify Ag, As, Cd, Cr, Cu, Mn, Ni, Pb, Rb, Sb, Sn, Ti, and V.

1.3.2. Water-soluble ion content

Anions and cations were extracted from 1/6th of each cellulose filter by leaching with a 30-min ultrasonic treatment: this step was repeated three times with 2–3 mL fresh ultrapure water and for each filter the solutions were finally gathered, filtered through a 0.45 porosity cellulose acetate membrane (Sartorius, Germany) and the volume adjusted up
to 20 mL. The resulting solution was analyzed by liquid ion chromatography for the quantification of NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻.

1.3.3. Total carbon
Total carbon quantification was performed using an elemental analyzer (CHNS/O FLASH 2000, Thermo Scientific, UK). About 30 mg of each quartz fiber filter was enclosed in two (25 mm × 25 mm) tinfoils using inox tweezers. The formed pellets were then introduced automatically in the elemental analyzer for total carbon (TC) quantification.

1.3.4. Measurement reliability and control
The whole analytical procedure including the sample preparation as well as the reliability of the measuring technique was validated considering standard reference materials: urban particulate matter NIST-SRM 1648 (National Institute of Standards and Technology, USA), soil (certificate 133317, Thermo Scientific®, UK) and cystine (certificate 134139, Thermo Scientific®, UK) certified materials. According to the methods described in Section 1.3.1 to 1.3.2, the SRM1648 was prepared for elemental, and ion analysis using ICP-MS, ICP-AES and ion chromatography respectively. TC certified soil and cystine samples were analyzed using the elemental analyzer. The recovery rates between obtained and certified values for the elemental quantification using ICP-AES and ICP-MS ranged from 92% to 106% with an exception for Cr (75%); for ion analysis, the recovery rate ranged between 94% and 102% whereas for TC, the analysis of the two certified materials gave 100% and 101% recovery rate.

Unexposed filters transported to the sampling site and placed 7 days in the sampler were used as “field blank” filters and measured following the same procedure used for the exposed filters. The mean value of the field blank filters was subtracted from the results of each exposed sample to obtain the best assessment of each element in the particulate matter.

1.4. Constrained weighted-non negative matrix factorization model

1.4.1. Description of the constrained weighted-non-negative factorization matrix
The model used in this study comes at this stage in the form of a weighted non-negative matrix factorization model and respects to a certain extent the maximum number of recommendations on the use of modeling in source apportionment studies. The constrained weighted non negative matrix factorization model used in this study has been developed at the University of Littoral Côte d’Opale, by the Laboratoire d’Informatique Signal et Image de la Côte d’Opale (LISIC) (Delmaire et al., 2010a, 2010b; Hleis, 2010).

Briefly, similar to the principles of positive matrix factorization, the non negative matrix factorization use the factorization approach of \( X = G \times F \) under positivity constraints \( (g_{ik} \geq 0) \) and \( (f_{jk} \geq 0) \), where the \( X \) matrix is the measured dataset, and \( G \) and \( F \) are the contribution and the source profile matrices respectively, \( g_{ik} \) and \( f_{jk} \) are elements from the \( G \) and \( F \) matrices. By default, the NMF algorithm does not consider any differed variance data in the calculations. Building a new version of the NMF that considers individual variances on the data input was essential and formed an important extension to the model. This upgrade is included in the “weighted NMF” based algorithm which enables the consideration of individual measurement uncertainties in the calculations (Delmaire et al., 2010a, 2010b; Hleis, 2010). The uncertainties are inserted in the model in a matrix form, and the calculation equation turns to the following form (Eq. (1)):

\[
\{ G, F \} = \arg\min_{G,F} \sum_{i=1}^{n} \sum_{j=1}^{n} \left( \frac{x_{ij} - (GF)_{ij}}{\sigma_{ij}} \right)^2
\]

where, \( x_{ij} \) represents the current element drawn from the observations matrix, \( G \) is the contributions matrix, \( F \) is the source profiles matrix, and \( \sigma_{ij} \) is the general element of the uncertainties matrix.

Furthermore, the weighted NMF algorithm has been modified in order to take into account the a-priori knowledge on the source chemical composition by applying constraints. In the so-called constrained weighted non negative factorization model, constraints are applied to the source profile composition in order to guide the calculation within iterations. Constraints can be inserted in two forms: the first one is the “equality” constraint which defines the presence or absence of an element in the source profile, and eventually forces its concentration to a specific value, as PMF/ME-2 (positive matrix factorization-multilinear engine 2) from USEPA (United States Environmental Protection Agency) can do (Norris et al., 2014; Paatero, 1999; Ramadan et al., 2003). The second type of constraint is “inequality” and imposes an order of abundance for a given species between the different source profiles (for example [X]source-1 > [X]source-2 and [X]source-3 > [X]source-4). These “inequality” constraints are preferred when compared to the equality ones because of their flexibility and lightness on the calculations. In fact, these soft constraints do not force the NMF model to calculate under stringent conditions, but only guide it to respect an order of abundance in species between the different source profiles. The accessibility to the NMF source code adds more advantages to this algorithm over the PMF, and allows additional developments and implementation compared to the PMF software which appears like a “black box”. Calculations using PMF are also known to be time consuming (Paatero and Tapper, 1994), whereas calculation times are lighter using the NMF algorithm (Gobinet, 2006). Finally, the use of constraints allows to refine source profiles and at the same time to be less subject to local minima during the calculation process.

The introduction of constraints constitutes a major advance in the source apportionment calculation field. Additional information about the constrained weighted NMF model is given in Delmaire et al. (2010b); Hleis (2010), and Kfoury et al. (2014).

1.4.2. Input data
The dataset includes the composition of 173 samples collected during November–December 2010 and March–April 2011 period at Dunkerque. The number of variable was 27 which correspond to the analyzed species concentrations recorded in the PM₁₅ samples, including major, minor and trace elements. Uncertainties on the data set were estimated by adding the error encountered during the whole analytical procedure. Errors on weight, on dilution, and on the effective surface of sampled
filters were estimated and, for each sample, were added to the relative standard deviation associated with the analytical results. Error on the atmospheric pressure and temperature corrected volume calculated by the Digitel DA80 sampler, estimated to 2%, was also considered. Uncertainties should be assessed relevantly to reflect the reliability of each data point (Liu et al., 2005) and the obtained uncertainties were majored of 10% for trace elements considering the bias observed on the SRM-1648 certified and obtained concentrations. Maximization of the uncertainties has been reported in numerous studies (Prendes et al., 1999).

Missing data were replaced by the mean value and the corresponding uncertainty was set to 400% and below detection-limit (DL) values were replaced by the DL/2 value, corresponding uncertainty was set to 400% and below detection-limit values were replaced by the DL/2 value, and associated with an uncertainty of 100% as it is commonly done in the matrix factorization data handling (Alleman et al., 2010; Kim et al., 2004; Liu et al., 2005; Polissar et al., 1998).

2. Results and discussion

2.1. PM$_{2.5}$ elemental mean concentrations

Metals, major ions and total carbon mean concentrations in PM$_{2.5}$ calculated for the winter and spring periods are given in Table 1. The PM$_{2.5}$ mean concentrations measured by the air quality network Atmo-Nord-Pas-de-Calais for the respective period are 24.9 and 33.2 μg/m$^3$. These average values are quite close to the 25 μg/m$^3$ annual concentration target value entered into force in 2010 and which is the limit value 2015 in Europe (EU directive 2008/50/EC). Furthermore, the daily PM$_{2.5}$ concentrations exceeded the 25 μg/m$^3$ daily limit value set by the air quality guidelines of the World Health Organization (WHO) up to 47% and 55% of the days during winter and spring periods respectively. The spring 2011 period has been marked by numerous PM$_{2.5}$ concentration peaks as the 33.2 μg/m$^3$ mean value shows. This latter is higher than the yearly limit value. Between the constituent, TC, NO$_3$, SO$_4$, and NH$_4$ dominate with values between 1.9 and 11.1 μg/m$^3$. When added to Cl$^-$ and Na, these six species explain 69% and 66% of the total PM$_{2.5}$ mass concentration in winter and spring respectively with various proportions between them. The numerous studies conducted to assess on the composition of PM$_{2.5}$ in northern European regions such as Ghent, Belgium (Viana et al., 2007), Goteborg, Sweden (Moloi et al., 2002), Rotterdam, Netherlands (Moobroek et al., 2011), West Midlands in United Kingdom (Harrison and Yin, 2010) also identified these six species as the major components of PM$_{2.5}$. Na and Cl$^-$ concentrations appears relatively constant between the winter and spring campaign. At the same time, the NO$_3$ concentrations is doubled from 5.7 to 11.0 μg/m$^3$ whereas the TC content decreases from 6.2 to 4.7 μg/m$^3$. These values are comparable to those observed in Ghent in the cold period (Viana et al., 2007), and the temperature plays a key role in the stabilization of NO$_3$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Winter (November–December, 2010)</th>
<th>Spring (March–April, 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.05 (A) 0.03 (G)</td>
<td>0.04 (A) 0.02 (G)</td>
</tr>
<tr>
<td>Al</td>
<td>17.8 (A) 14.2 (G)</td>
<td>27.8 (A) 23.1 (G)</td>
</tr>
<tr>
<td>As</td>
<td>0.91 (A) 0.85 (G)</td>
<td>0.77 (A) 0.65 (G)</td>
</tr>
<tr>
<td>Ba</td>
<td>0.90 (A) 0.77 (G)</td>
<td>0.77 (A) 0.70 (G)</td>
</tr>
<tr>
<td>Ca</td>
<td>49.5 (A) 40.5 (G)</td>
<td>65.1 (A) 56.1 (G)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.30 (A) 0.16 (G)</td>
<td>0.35 (A) 0.18 (G)</td>
</tr>
<tr>
<td>Cr</td>
<td>1.43 (A) 0.78 (G)</td>
<td>1.23 (A) 0.80 (G)</td>
</tr>
<tr>
<td>Cu</td>
<td>2.74 (A) 1.81 (G)</td>
<td>2.26 (A) 1.65 (G)</td>
</tr>
<tr>
<td>Fe</td>
<td>92.9 (A) 58.1 (G)</td>
<td>101 (A) 61.8 (G)</td>
</tr>
<tr>
<td>K</td>
<td>132 (A) 113 (G)</td>
<td>98.9 (A) 82.4 (G)</td>
</tr>
<tr>
<td>Mg</td>
<td>34.2 (A) 18.7 (G)</td>
<td>42.2 (A) 26.1 (G)</td>
</tr>
<tr>
<td>Mn</td>
<td>7.19 (A) 2.76 (G)</td>
<td>8.11 (A) 3.26 (G)</td>
</tr>
<tr>
<td>Na</td>
<td>237 (A) 150 (G)</td>
<td>240 (A) 150 (G)</td>
</tr>
<tr>
<td>Ni</td>
<td>3.23 (A) 2.23 (G)</td>
<td>4.63 (A) 3.29 (G)</td>
</tr>
<tr>
<td>P</td>
<td>10.54 (A) 7.20 (G)</td>
<td>16.4 (A) 8.58 (G)</td>
</tr>
<tr>
<td>Pb</td>
<td>13.90 (A) 9.59 (G)</td>
<td>9.77 (A) 6.96 (G)</td>
</tr>
<tr>
<td>Rb</td>
<td>0.45 (A) 0.33 (G)</td>
<td>0.42 (A) 0.30 (G)</td>
</tr>
<tr>
<td>Sb</td>
<td>1.07 (A) 0.71 (G)</td>
<td>0.79 (A) 0.46 (G)</td>
</tr>
<tr>
<td>Sn</td>
<td>1.37 (A) 0.88 (G)</td>
<td>1.01 (A) 0.76 (G)</td>
</tr>
<tr>
<td>Sr</td>
<td>0.36 (A) 0.31 (G)</td>
<td>0.37 (A) 0.32 (G)</td>
</tr>
<tr>
<td>Ti</td>
<td>1.00 (A) 0.02 (G)</td>
<td>2.22 (A) 1.13 (G)</td>
</tr>
<tr>
<td>V</td>
<td>1.71 (A) 1.34 (G)</td>
<td>6.35 (A) 4.25 (G)</td>
</tr>
<tr>
<td>Zn</td>
<td>38.7 (A) 22.7 (G)</td>
<td>44.0 (A) 19.4 (G)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Winter (November–December, 2010)</th>
<th>Spring (March–April, 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$</td>
<td>1914 (A) 1645 (G)</td>
<td>2306 (A) 2000 (G)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>580 (A) 508 (G)</td>
<td>543 (A) 453 (G)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>5707 (A) 3782 (G)</td>
<td>11,064 (A) 7581 (G)</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>2521 (A) 2011 (G)</td>
<td>2854 (A) 2425 (G)</td>
</tr>
<tr>
<td>TC</td>
<td>6198 (A) 4884 (G)</td>
<td>4727 (A) 4090 (G)</td>
</tr>
</tbody>
</table>

μA: arithmetic mean; μG: geometric mean; SD: standard deviation; n: number of samples.
species. Trace metal concentrations ranges from some hundreds of pg/m$^3$ to some tens of ng/m$^3$ and few variations of mean concentration levels are observed for these species between the two studied periods. Nevertheless, large standard deviation values are observed and indicate the high variability of the concentration depending on the meteorological conditions.

### 2.2. Evidencing local sources of emissions

#### 2.2.1. Concentrations roses

The concentration roses calculated for 18 selected species using data recorded for both winter and spring campaign are illustrated in Fig. 2. By meaning the calculation on a large number of samples, such a representation allows the identification of the wind direction under which the maximum concentrations are recorded. A first conclusion can be quickly drawn from the roses' pattern and four groups of elements can be distinguished. The first group encloses Ag, Al, As, Ca, Cd, Fe, Mn, Pb, and Rb elements, which clearly shows maximum concentrations for winds blowing from the east-northwest sector which represent the ISW influence. These elements have been previously identified in raw materials and dust collected inside the ISW. They were proposed as possible tracers of the ISW emissions (Heis et al., 2013). The second group is constituted by Zn and Cr which concentration roses evidence a maximum from the east direction. Such elements appear to be specific to the activity of the electric steel plant located at 7 km east of the sampling site. In a previous study, this high Zn contribution was also observed in a coastal site located 10 km southwest from the electric steel plant (Ledoux et al., 2006). Some elements of the first group such as Ag, Cd, Fe, Ni, Pb, Ba, and Cu give also a contribution when the wind is blowing from the east and could be considered as a common marker of the steelmaking activity. The third group includes Sn, Sb, K and Cu, which have maximum concentrations with wind blowing from the south-southwest direction corresponding to the urban sector. Such trace elements have been reported in several studies and were linked to the traffic sources (Amato et al., 2009). Finally, Ni and V concentration roses exhibited similar shapes with a maximum from the west-southwest and north-northeast wind sector. The origin of such elements is widely documented and linked to heavy fuel oil combustion (Vallius et al., 2005; Wu et al., 2007). In the study area, the maritime traffic is one of the highest in the world: up to 800 ships sail each day from the English Channel to reach the North Sea. It should be pointed out that the English Channel is in W-SW direction of the sampling point. Then the maximum for Ni and V concentration roses observed from the W-SW wind sector could be linked to heavy fuel oil combustion in the English Channel. From the N-NE direction, the Ni and V detected in particulate samples could also be assumed to come from ships without neglecting the refinery activities located in Dunkerque.

The metal concentration roses clearly evidence the influence of the ESP and the ISW on the PM$_{2.5}$ composition at Dunkerque and it should be interesting to push the investigation further to identify emission tracers.

#### 2.2.2. Diagnostic ratios for wind sectors under industrial influence

In order to distinguish between the effects of the different industrial emissions having an influence on ambient metal concentration, a specific selection of samples collected downwind of industrial sites was achieved (Fig. 1). Metal concentration data were studied carefully in an attempt to determine if a specific ratio between the elements could reveal an influence of industrial activities on PM$_{2.5}$ composition. Therefore, different trace elements were selected such as Fe, K, Zn, Cr, Mn, Ni, Cu, Rb, Cd and Pb. Indeed, daily PM composition data showed that higher concentrations of these elements could be observed for wind blowing from the industrial sectors (Fig. 2). In addition, in a

![Fig. 2 – Mean elemental concentration roses calculated for the winter and spring campaign at Dunkerque (units: ng/m$^3$).](image-url)
previous work, we have evidenced that most of these elements were emitted from iron and steelwork facilities (Helis et al., 2013). The latter study shows that the facilities release particles with different physico-chemical characteristics with each one related to a specific section within the steelmaking processes. Indeed, emissions from the ore sintering stack, a major particulate emitter, were enriched in K, Cr, Fe, Na and Pb, whereas diffuse emissions from the steelmaking area were characterized by high amounts of Fe, Zn and Mn. Moreover, the electric steel plant located to the east of the PM sampling site significantly accounts for the emission of Zn, Cr, Pb, Ni and Cu (E-PRTR, 2012).

The selection of samples under industrial influences was achieved considering the background concentration level which corresponds to the geometric mean concentration, which gives less impact to values distant from the central tendency. Fe, K and Zn concentrations were taken into account to select the samples highly impacted by steelmaking activities. The geometric mean concentrations for Fe, K, Zn were estimated to 60, 90 and 20 ng/m$^3$, respectively during the whole period. It was decided to use samples which are further from the background level by considering a threshold concentration value equals to 100 ng/m$^3$ for Fe and K and 50 ng/m$^3$ for Zn. Two sectors were defined:

1. The 250–320° wind sector under the integrated steelworks influence. The samples with Fe concentration above 100 ng/m$^3$ or K concentration above 100 ng/m$^3$ were selected ($n = 20$ samples); 
2. The 30–90° wind sector under the electric steel plant influence. The selected samples have Zn concentration above 50 ng/m$^3$ ($n = 12$ samples).

Table 2 regroups values of average, minimum and maximum concentration for selected PM$_{2.5}$ samples collected downwind of the industrial sectors. Under the wind of the two industrial sectors, most of the selected metals show higher average concentration values compared to the average concentration including all wind directions. This observation is not encountered in the case of K and Cr which can be emitted by other sources such as biomass combustion (Ilacqua et al., 2007; Orru et al., 2010) and brake wear (Gietl et al., 2010). The comparison between the two industrial sectors revealed higher average concentration of Zn, Cu and Pb downwind of the electric steel plant and Fe, Mn, Ni, Rb and Cd downwind of the integrated steel works. In this last case, we observed two kinds of samples: a first group relatively enriched in K, Pb, and Rb whose emissions can be related to the ore sintering process, and a second one enriched in Fe, Zn, Cr, Ni and Cu, related to diffuse emissions from steelmaking (Kfoury, 2013). Similar results have been generally observed in integrated steelworks units (Dall’Osto et al., 2008; Lamaison, 2006; Machemer, 2004; Oravistejärvi et al., 2003; Sammut et al., 2006).

In a second step, calculation of element ratios downwind of the industries were proposed and compared to the values obtained using all the samples regardless of the wind direction (Table 3). The results indicate that Zn/Fe and Zn/Mn ratios allow a clear separation between the integrated steelwork influence ($Zn/Fe = 0.1; Zn/Mn = 1.7$) and the electric steel plant ($Zn/Fe = 1.1; Zn/Mn = 10$). The ratios for ISW are clearly lower than the average ratios relative of all wind sectors ($Zn/Fe = 0.4; Zn/Mn = 5.6$) whereas those for ESP are clearly higher. Using a similar approach, the Cr/Cd (1.3 for ISW and 16 for ESP) and Pb/Cd ratios (16 for ISW and 77 for ESP) can be considered as specific tracers of the corresponding sources. The high proportion of Zn and Pb evidenced for the ESP site is related to the significant release of metals with low melting points from the electric arc furnace used for smelting of steel scrap. Furthermore, ratios considering Cr indicate a higher proportion of Cr under 30–90° wind sector related to the production of the special steel in the ESP site.

A deeper analysis of PM$_{2.5}$ composition under the ISW sector was attempted in order to differentiate between different particles sources at this site. Samples with high K concentrations compared to Fe, which reveals potential influence of the sintering stack source, were considered. It allows the

<table>
<thead>
<tr>
<th>Element</th>
<th>250–320° wind sector ($n = 20$ samples)</th>
<th>30–90° wind sector ($n = 12$ samples)</th>
<th>All wind sectors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Fe</td>
<td>312</td>
<td>103</td>
<td>1542</td>
</tr>
<tr>
<td>K</td>
<td>127</td>
<td>49</td>
<td>358</td>
</tr>
<tr>
<td>Zn</td>
<td>49</td>
<td>8.4</td>
<td>174</td>
</tr>
<tr>
<td>Cr</td>
<td>1.3</td>
<td>0.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Mn</td>
<td>30</td>
<td>7.8</td>
<td>92</td>
</tr>
<tr>
<td>Ni</td>
<td>6.0</td>
<td>2.1</td>
<td>16.9</td>
</tr>
<tr>
<td>Cu</td>
<td>2.8</td>
<td>0.8</td>
<td>9.6</td>
</tr>
<tr>
<td>Rb</td>
<td>1.1</td>
<td>0.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Cd</td>
<td>1.0</td>
<td>0.1</td>
<td>8.0</td>
</tr>
<tr>
<td>Pb</td>
<td>16.3</td>
<td>6.0</td>
<td>37</td>
</tr>
</tbody>
</table>
consideration of relatively high values of Rb/Cr and Pb/Cr but low values of Cu/Cd as indicators of the influence of the sintering process emissions (Table 3). However, it appears that the higher value of Zn/Mn under 250–320° wind sector could be linked to a potential influence of the steel making process among the integrated steelworks complex.

2.3. Constrained weighted non-negative matrix factorization

2.3.1. A priori knowledge and number of sources

The CW-NMF hybrid receptor model allows the user to take into account a priori knowledge on source profile by applying constraints. Thus, the first step is to identify the sources that clearly influence the PM$_{2.5}$ composition and to collect the maximum of information in order to build the constraints matrix. This initial number of sources will form a starting point for the calculations and then, step by step, the number of sources is increased (in parallel the constraints could be modified) until satisfying result obtained.

Dunkerque city is potentially influenced by different sources of PM$_{2.5}$ emissions. Between them, the marine source is evident due to the proximity of the sea. Crustal dust linked to soil erosion makes another natural source of particulate matter. The urban activity constitutes another potential source and contributes essentially within the forms of traffic and residential activities. Secondary nitrates and secondary sulfates are commonly identified in all PM$_{2.5}$ characterization studies. In addition to the natural and anthropogenic sources mentioned earlier, we have demonstrated (in Section 2.2) that emissions from the ISW, with the two typical signature of sintering stack and fugitive emissions, and ESP can be qualitatively identified in some PM$_{2.5}$ samples. This result forces us to consider three more source profiles in order to take into account the steelmaking activity in Dunkerque. Consequently, more than 10 factors can be proposed: sea-salts with the distinction between “fresh sea-salts” and “aged sea-salts”; “crustal” source; “secondary nitrates” and “secondary sulfates”; traffic with the distinction between the “non-exhaust” emission related to the abrasion of mobile parts of the car (tires, brakes, etc.) and exhaust emission named hereafter “combustion” source; a second combustion source which take into account the “heavy fuel oil combustion” evidenced by the Ni and V concentration roses; finally, we add ISW sintering stack, ISW fugitive emissions and ESP as discussed earlier.

Constraints for the considered factors were deduced from the literature (Amato et al., 2009; Mooibroek et al., 2011; Moreno et al., 2013; Schauer et al., 2006; Vallius et al., 2005; Wu et al., 2007). It includes the composition of sea-water and continental crust (Wedepohl, 1995) for natural and urban background sources, the analysis of raw materials, the characterization of dust collected inside or directly under the influence of the facilities (Hleis, 2010; Hleis et al., 2013). This significant load of information was intentionally used in the model because it will efficiently guide the calculation process to result in refined results, mostly when modeling complicated cases such as our study.

2.3.2. Source profiles

Different scenarios have been tested while considering our a-priori knowledge on the sources around the site. Several preliminary CW-NMF runs evidenced that the best results are obtained when considering 11 factors. The normalized profiles of the 11 identified sources are given in Fig. 4.

(1) Marine aerosols. The two first profiles are related to marine aerosols with a distinction between the freshly emitted “sea-salts” and the “aged sea-salts”. The presence of high loads of Na and Cl$^-$, as well as some major metals (Ca, K and Mg) and sulfate ions constituted a signature of the first profile. The second profile is also characterized by a high proportion of Na, with a significantly less contribution of Cl$^-$. This chloride depletion is balanced by an enrichment of nitrates and sulfates which is a well-known chemical reaction between gaseous species and sea-salts (Seinfeld and Pandis, 2006). The obtained “aged sea-salts” profile evidenced some trace metals contribution such as Cr, Ni, and V, which evidence an anthropogenic contribution. Ni and V have been cited as a marker of shipping activity, and in particular fuel oil combustion (Sippula et al., 2007).

(2) Crustal. Major elements like Al, Ca, Fe, K, and Mg are found at the highest levels in the third profile with also various trace element contribution which is in accordance with the crustal source profiles found in the literature (Mooibroek et al., 2011; Moreno et al., 2013).

(3) Secondary inorganic aerosols (SIA). It included two profiles showing on one hand high contribution of SO$_4^{2-}$ and NH$_4^+$, and on the other hand NO$_3^-$ and NH$_4^+$ are identified as “secondary sulfates” and “secondary nitrates”, respectively. In addition, these profiles contain small contribution of trace metal, such as Pb and Zn, and Cl$^-$ and TC which are found in weak to moderate amounts. In particular, TC contribution is evidenced in the “secondary nitrates” profile and not in the “secondary sulfates”. In the literature, the presence of TC in SIA profiles has been assigned to the aging of SIA and/or the effect of mixing with particles from combustion sources (Cusack et al., 2013; Koçak et al., 2015; Pey et al., 2013). Koçak et al. (2015) observed a moderate correlation between NO$_3^-$ and TC, the absence of correlation between SO$_4^{2-}$ and TC, and also ascribed the NO$_3^-$–TC relation to the combustion process. Due to the NO$_3^-$ and TC dependence, this conclusion could explain why TC is only detected in the “secondary nitrates” and not in the “secondary sulfates” profile. Consequently, we cannot exclude here that the “secondary nitrates” profile contains also some characteristics of combustion source at a weaker extent. Nevertheless, the model appears to have the ability to distinguish the two categories of SIA which satisfies the recommendations of Viana et al. (2008) concerning the source apportionment studies.

(4) Combustion. This type of profiles is found characterized by TC contribution between 70% and 80%. Two types of combustion are evidenced, within “Combustion 1” and “Combustion 2”. Both profiles show high amounts of TC, but are also enriched in NO$_3^-$ and NH$_4^+$ in addition to some differences for trace elements between the profiles. Ni and V are present in “Combustion 1” which shows the impact of oil combustion in this profile (Amato et al., 2009; Mooibroek et al., 2011; Vallius et al., 2007).
Fig. 3 – Constrained weighted non-negative matrix factorization (CW-NMF) calculated versus observed concentrations for all the species considered in the matrix factorization calculation.
Traffic non-exhaust. This profile is a typical trace element profile with various amounts of Fe, Zn, Sn, Sb, Zn, Cr, Al, Pb, Ni, Mn, and Cu without any ionic or carbon species contribution. It is not always detected in the source apportionment studies involving matrix factorization and is quite often called “metals” without any further identification. Nevertheless, some authors reported such traffic related metal profile by assigning the contribution of a large variety of metal such as Cu, Sb, Fe, Zn, Al, Ca, Cr, Ni, Pb, Ti, V, K, Cd, Mn, Sn and Sr (Amato et al., 2009; Schauer et al., 2006). The characteristics of the identified profile are also in accordance with the results mentioned in a study focusing on the metallic and mineral dust in urban areas (Moreno et al., 2013) and also with the review on non-exhaust particulate matter from road traffic (Thorpe and Harrison, 2008).

(5) Traffic non-exhaust. This profile is a typical trace element profile with various amounts of Fe, Zn, Sn, Sb, Zn, Cr, Al, Pb, Ni, Mn, and Cu without any ionic or carbon species contribution. It is not always detected in the source apportionment studies involving matrix factorization and is quite often called “metals” without any further identification. Nevertheless, some authors reported such traffic related metal profile by assigning the contribution of a large variety of metal such as Cu, Sb, Fe, Zn, Al, Ca, Cr, Ni, Pb, Ti, V, K, Cd, Mn, Sn and Sr (Amato et al., 2009; Schauer et al., 2006). The characteristics of the identified profile are also in accordance with the results mentioned in a study focusing on the metallic and mineral dust in urban areas (Moreno et al., 2013) and also with the review on non-exhaust particulate matter from road traffic (Thorpe and Harrison, 2008).

(6) In addition to these 8 coastal and urban background profiles, 3 supplementary profiles related to the steel-making local activities were identified as the integrated...
steelworks main emissions, namely ISW-fugitive and ISW-sintering stack, and the nearby electric steel plant emissions.

(7) ISW fugitive and ISW sintering stack. The two ISW profiles conserved similar characteristics compared to samples collected at the emission point inside the integrated steelworks. High levels of Fe, Ca, Al, Zn, Na, Pb and Mn were respected as well as the presence of nitrates and sulfates in the fugitive emissions. On the other hand, we found that the absence of Mg in the two ISW profiles constitutes an unexpected result (Hleis et al., 2013). Furthermore, the sintering stack emissions profile respected to a certain extent the chemical composition of these emissions with the presence of Fe, K, Pb, Cd, Rb, Cl⁻ and NH₄⁺ (Hleis et al., 2013). These results remain however in accordance with another study in which the application of PMF revealed the same elements that characterized the sintering activities at the same site (Alleman et al., 2010). These differences between the knowledge on the sources’ composition and the calculated ones remain moderate, since the species exhibiting these variations do not constitute the basis for the profiles identification.

(8) Electric steel plant. In this last calculated profile, Zn is a major component, followed by Fe, Mg, Ca, Mn, Pb, Cr and Cu which are all found high to fairly concentrated in the calculated profile. This composition respects to a high extent the composition characteristics of the ESP influenced PM₂.₅ as demonstrated in Section 2.2.

2.3.3. Correlation between observed and calculated values
Correlations between observed and calculated values have been investigated in order to insure that qualitative and quantitative interpretations of the modeled results can be done with a high level of confidence. First, the total calculated concentrations in both winter and spring correlated very well ($R^2 = 0.99$) with the corresponding total observed concentrations (Fig. 3). The slope value 1.01 is the proof that the total species concentration in PM₂.₅ is also very well estimated.

Fig. 5 – Distribution of the chemical species between the 11 sources identified at Dunkerque using the CW-NMF.

Fig. 6 – Mean source contributions in PM₂.₅ collected at Dunkerque during the winter and the spring season.
A deeper examination using the reconstruction of individual species has been also conducted (Fig. 3) and allows us to conclude that major anions concentrations are very well reconstructed with a correlation coefficient and a ratio between recalculated and observed values very close to 1. Correlations for TC and NH$_4^+$ remains very acceptable with a correlation coefficient $R^2$ of 0.76 and 0.81 and a ratio value of 1.03 and 0.85 respectively. The remaining metal’s calculated and observed concentrations were found well correlated: $R^2$ values are mainly above 0.80, and ratio value ranges from 0.72 for Na to 0.99 for Ni excepted for Cd, Mn and As (0.42 < $R^2$ < 0.55). For Ag and Ti, the model does not appear able to correctly place these two elements in the profile or to properly estimate the source contribution as the correlation between calculated and observed values appear weak and the corresponding ratio is far from 1. The contribution of Ti and Ag is drastically underestimated, thus the discussion on Ti and Ag origin will be omitted from the upcoming sections.

2.3.4. Origin of chemical species

By considering the mean contribution and the composition of each source, it is possible to determine which source contributes most in the load of a given chemical species. This calculation was only achieved for species which concentration data are well reconstructed by the model; Ag and Ti were then excluded.

As shown in Fig. 5, elements are found well distributed between the sources. The “sea-salts” source contributed in most of Na and Cl$^-$. “Aged sea-salts” profile is found to contribute importantly in Na and majorly in Mg but also in Ca, and Sr loads. The “crustal” profile participated in important percentages of Al, Ca, Ba loads. SO$_4^{2-}$ and NO$_3^-$ found their major origin in the SIA sources, and NH$_4^+$ is mainly found in the form of “secondary nitrates”.

The “heavy fuel oil combustion” explains 86% and 72% of the observed V and Ni concentration respectively and also a part of the detected Cr. The second combustion profile (Combustion 2) contributes in a large amount of various species, i.e., 78% of TC, more than 30% of K, Ba, and NH$_4^+$, also few contribution in Al, Ca, Cu, Pb, Sr, Sb and Sn are found mainly linked to the “traffic non-exhaust” source.

Finally, the industrial influences are found to participate in most of the trace metals. The “ISW-fugitive” profile is contributing in the major loads of Fe, As and Mn, as well as partial percentages of Al, Ca, Cr, Cu, Ni, Pb, Rb, V and Zn. The “ISW-sintering stack” contributes mainly to Cd, Pb, Rb and Cl$^-$. PM$_{2.5}$ atmospheric concentrations. Finally, the “electric steel plant” contributes the most to the Zn, Cr, Cu and Mn loads.

2.3.5. Source contributions

The CW-NMF was performed using a dataset enclosing spring and winter PM$_{2.5}$ samples, which allows to quantify the contribution of all 11 sources evidenced for each of the winter and spring samples. From these results, individual contributions of PM$_{2.5}$ sources were grouped for the winter and spring data. The mean contribution of the eleven sources to the total PM$_{2.5}$ content for the winter and spring period are given in Fig. 6.

Three sources appear to be responsible of the major part of PM$_{2.5}$ observed during both seasons: combustion sources, secondary nitrates and secondary sulfates. Their global contribution is estimated to be 93% in winter as well as in spring but the distribution between the three sources is quite different. During the winter period, combustion emissions contributed the most (44%), followed by secondary nitrates (34%) and secondary sulfates (15%), while in the spring campaign a major contribution from the secondary nitrates profile (62%) is recorded, followed by the combustion source (20%) and the secondary sulfates (12%), which seasonal contribution remains relatively constant.

When compared to the winter season, the combustion source contribution decreases from 45% (winter) to 20% (spring). As mentioned earlier, we were not able to distinguish traffic related combustion from domestic heating combustion sources. Nevertheless, an estimation of this latter contribution can be suggested based on this result. In fact, the difference between the two combustion sources contributions for the two seasons could probably be linked to the decrease in the use of heating combustion in the spring during which higher temperatures were recorded. Assuming that the impact of traffic source combustion remains constant between the two seasons, the contribution of heating combustion sources can be estimated to be at least 25% in winter.

When adding secondary nitrates to secondary sulfates, secondary inorganic aerosols appear as the major contributor to the PM$_{2.5}$ load explaining about 49% in winter and 73% in summer. Such values are comparable with those calculated in The Netherlands using PMF and showing a proportion of SIA in PM$_{2.5}$ varying between 61% and 74% on a yearly basis (Mooibroek et al., 2011). In the present study, SIA are found mainly in the form of nitrates in spring, but its distribution between nitrates and sulfates profiles is much less defined in winter. Many PM$_{2.5}$ concentration peaks were recorded in spring and the high SIA contributions found can be highly related to the accumulation phenomena and long range transport. A deeper investigation using air mass back-trajectories showed that highest SIA concentrations are related to the Eastern and Central Europe origin (Kfoury, 2013).

The other eight evidenced sources only contribute in 7% of the PM$_{2.5}$ concentration in total with few seasonal differences. Between them, sea-salts and aged sea-salts contribute the most with 2.9% and 1.9% in winter and 2.5% and 1.8% in spring, respectively. Marine aerosols are generally large particles, which can explain the relatively low contribution to the PM$_{2.5}$ load despite of the site location in the vicinity of the sea. Finally, the average contribution of the integrated steelworks was about 1.6% and 1.3%, including fugitive (0.5%) and sintering stack (0.8% to 1.1%). These values are consistent with a study performed in 2008 where the mean contribution of ISW to the PM$_{10}$ concentration in Dunkerque was estimated to be 3% with daily peaks reaching 17% (Heis, 2010). The contribution of the ESP emissions to PM$_{2.5}$ load is estimated to be 0.3%. Heavy fuel oil combustion contribution was estimated to be 0.3% and 0.8% according to the season, whereas crustal and traffic non-exhaust sources gave lower contributions to the PM$_{2.5}$ load.

The steel making activity in Dunkerque has an impact estimated to range from 1.6% to 1.9%, which are relatively low values, if we consider the industrial presence. Nevertheless, as shown in Section 2.2 and Fig. 5, the industrial activities have a real impact on the PM$_{2.5}$ composition and contribute at
a high level to specific metals concentrations that are directly linked to industrial activities.

3. Conclusion

The monitoring of PM$_{2.5}$ and the determination of its chemical composition was achieved in an industrialized city located in northern France. It was observed that daily PM$_{2.5}$ concentrations exceeded the value of 25 μg/m$^3$ during 47% and 55% of the days in the 2010–2011 winter and spring periods respectively. NO$_x$, SO$_4$$^2$−, NH$_4^+$ and TC were found as the major components of PM$_{2.5}$ and significant seasonal differences were evidenced. A higher proportion of TC was measured in winter compared to spring and was explained partly by higher emissions related to heating devices during the cold period. However, secondary inorganic aerosols, mainly nitrates, dominated the PM$_{2.5}$ composition in the spring period which is in agreement with previous observations in north-west Europe.

The originality of the study lies within the procedure used to track the impact of industrial emissions using trace metals. Metal concentration roses were successfully used to evidence metallic species such as Fe, Zn, Mn, Pb, Cd, Cr and Rb which could be used as tracers of steelworks emitters. This approach was complemented by the proposal of diagnostic ratios allowing the distinction between different emitters in the context of a multi-sources industrial influence. Zn/Fe and Zn/Mn ratios were shown to allow a clear separation between the integrated steelworks (ISW) influence (Zn/Fe = 0.1; Zn/Mn = 1.7) and the electric steel plant (ESP) one (Zn/Fe = 1.1; Zn/Mn = 10). Furthermore, the impact of the sintering stack emissions from the ISW site was distinguished by high Rb/Cr and Pb/Cr and low Cu/Cd ratio values.

The knowledge on source tracers and on the relative composition of the different sources was used as a priori information when running the constrained weighted non-negative matrix factorization (CW-NMF) model. Our approach allows the separation between 11 different chemical profiles, 3 of which are assigned to steelworks facilities emissions. The separation of industrial sources was particularly challenging due to the presence of similar chemical elements in the corresponding source profiles. Our study evidenced that these industrial sources have a low contribution to the PM$_{2.5}$ concentration but a relatively large one in Fe, Zn, Mn, Pb, Cd, Cr and Rb concentrations. Up to our knowledge, this work proposed for the first time the use of a priori information in a hybrid receptor model based on a matrix factorization method and taking into account soft constraints on chemical profiles.

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