Receptor modelling of airborne particulate matter in the vicinity of a major steelworks site

Taiwo, Adewale; Beddows, David; Calzolai, G.; Harrison, Roy; Lucarelli, F.; Nava, S.; Shi, Zongbo; Valli, G.; Vecchi, R.

DOI: 10.1016/j.scitotenv.2014.04.118

License: Other (please specify with Rights Statement)

Document Version
Peer reviewed version

Citation for published version (Harvard):

Download date: 21. Dec. 2018
Receptor Modelling of Airborne Particulate Matter in the Vicinity of a Major Steelworks Site

A.M. Taiwo¹, D.C.S. Beddows¹, G. Calzolai⁴,⁵
Roy M. Harrison¹‡, F. Lucarelli⁴,⁵, S. Nava⁵, Z. Shi¹
G. Valli²,³, R. Vecchi²,³

¹Division of Environmental Health & Risk Management
School of Geography, Earth & Environmental Sciences
University of Birmingham
Edgbaston, Birmingham, B15 2TT
United Kingdom

²Department of Physics
Università degli Studi di Milano & INFN-Milano
Via Celoria 16, 20133 Milan, Italy

³INFN-Milano
Via Celoria 16, 20133 Milan, Italy

⁴Department of Physics and Astronomy
Università degli Studi di Firenze
Via Sansone 1, 50019 Florence, Italy

⁵INFN-Firenze
Via Sansone 1, 50019 Florence, Italy

*Corresponding Author: r.m.harrison@bham.ac.uk

† Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, 21589, Saudi Arabia
HIGHLIGHTS

- Air sampling has taken place at 4 sites around the steelworks.
- Hourly and daily samples were collected with Streaker and Partisol samplers.
- ME-2 was applied to both datasets for source apportionment.
- PM contributions from individual steelworks processes are identified.
- Steelworks emissions account for 45% of measured PM$_{10}$ mass.
ABSTRACT

In this study, the Multilinear Engine (ME-2) receptor model was applied to speciated particulate matter concentration data collected with two different measuring instruments upwind and downwind of a steelworks complex in Port Talbot, South Wales, United Kingdom. Hourly and daily PM samples were collected with Streaker and Partisol samplers, respectively, during a one month sampling campaign between April 18 and May 16, 2012. Daily samples (PM$_{10}$, PM$_{2.5}$, PM$_{2.5-10}$) were analysed for trace metals and water-soluble ions using standard procedures. Hourly samples (PM$_{2.5}$ and PM$_{2.5-10}$) were assayed for 22 elements by Particle Induced X-ray Emission (PIXE).

PM$_{10}$ data analysis using ME-2 resolved 6 factors from both datasets identifying different steel processing units including emissions from the blast furnaces (BF), the basic oxygen furnace steelmaking plant (BOS), the coke-making plant, and the sinter plant. Steelworks emissions were the main contributors to PM$_{10}$ accounting for 45% of the mass when including also secondary aerosol. The blast furnaces were the largest emitter of primary PM$_{10}$ in the study area, explaining about one-fifth of the mass. Other source contributions to PM$_{10}$ were from marine aerosol (28%), traffic (16%), and background aerosol (11%). ME-2 analysis was also performed on daily PM$_{2.5}$ and PM$_{2.5-10}$ data resolving 7 and 6 factors, respectively. The largest contributions to PM$_{2.5-10}$ were from marine aerosol (30%) and blast furnace emissions (28%). Secondary components explained one-half of PM$_{2.5}$ mass. The influence of steelworks sources on ambient particulate matter at Port Talbot was distinguishable for several separate processing sections within the steelworks in all PM fractions.

Keywords: Steelworks; source apportionment; ME-2; hourly resolution; receptor modelling
1. INTRODUCTION

Both acute and chronic exposures to airborne particulate matter (PM) have been associated with adverse effects upon health including premature mortality (Pope and Dockery, 2006). Consequently, the World Health Organisation (WHO, 2006) recommends strict guidelines for airborne particulate matter measured both as PM$_{10}$ and PM$_{2.5}$. Governments around the world are developing and applying abatement strategies to reduce population exposures to particulate matter. The development of cost-effective strategies depends critically upon a quantitative knowledge of the contribution of different sources to airborne particulate matter concentrations. Receptor modelling is a widespread approach to identify emission sources and to resolve their contribution to PM mass (Viana et al., 2008a).

For many years the town of Port Talbot has suffered some of the worst air quality in the United Kingdom (AQEG, 2011). The basic operational steelworks units in Port Talbot are coke making, sintering, blast furnace, basic oxygen furnace and other steel processing units (Passant et al., 2002). Earlier work (Moreno et al., 2004; Dall’Osto et al., 2008; Hayes and Chatterton, 2009) has identified the steelworks as a major contributor to local PM$_{10}$ concentrations and the steelworks units have been recognised as major emission sources of heavy metals such as chromium, copper, lead, cadmium, arsenic, zinc, manganese, iron, nickel, vanadium and selenium (Passant et al., 2002; Moreno et al., 2004; Dall’Osto et al., 2008). However, knowledge has been lacking as to the magnitude of the contribution of the steelworks to airborne PM concentrations as well as the identity of the predominant sources within the steelworks.

The present study focuses on the identification and apportionment of emission sources of particulate matter pollution in the vicinity of the integrated steelworks complex located in Port Talbot. As a complement to previous studies, which used approaches including scanning electron microscopy (Moreno et al., 2004), single particle analysis using an aerosol time of flight mass...
spectrometer (Dall’Osto et al., 2008; 2012) and particle size distribution analysis (Taiwo et al., 2014), the present study has applied the Multilinear Engine (ME-2) receptor model to identify and apportion emission sources of PM in the study area. The aim was not only to identify the steel emission profiles, but also to attribute emissions to specific production units in the integrated steel complex.

2. MATERIALS AND METHODS

The study area is the coastal industrial town of Port Talbot (51°34’N and 3°46’W) located in South Wales, UK. The integrated iron and steel facility is the largest steel producer in the UK and one of the biggest steel producers in Europe, with a production capacity of about 5 million tonnes per year. It is a complex mixture of stationary source and fugitive emissions associated with the main processes which consists of iron-making (sintering, blast furnace BF, and raw materials), steel-making (basic oxygen steel-making BOS and coking) and rolling mills (hot and cold) processing (Passant et al., 2002). Traditional particle sampling techniques do not have sufficient time resolution to capture short-lived emission events arising from specific operations; therefore, in this work we coupled hourly and daily resolution sampling (Lucarelli et al., 2011).

Four monitoring sites [Fire Station (FS), Prince Street (PS), Dyffryn School (DS) and Little Warren (LW)] were selected within the study area for dichotomous Partisol (daily sampling) samplers, while Streaker (hourly sampling) samplers were placed at two sites (FS and LW). The Little Warren sampling location was adopted as the background site, due to the prevailing south-westerly winds and its typically upwind position (Figure 1). The sites were selected to provide different directions from steelworks processes in order to assist differentiation of the emission sources.
2.1 Sampling and Analysis

The hourly and daily sampling of PM was achieved through the use of Streaker and Dichotomous Partisol 2025D samplers for a period of 29 days between April 18 and May 16, 2012.

Streaker samples (collected on Nuclepore filters for PM$_{2.5}$ and Kapton foils for PM$_{2.5-10}$) were analysed by Particle Induced X-ray Emission (PIXE) at the 3 MV Tandetron accelerator facility of the INFN-LABEC laboratory in Florence, Italy. Twenty-two elements from sodium to lead were analysed in both fine and coarse Streaker PM samples. Details of the Streaker sampler and PIXE analysis have been extensively reported elsewhere (D’Alessandro et al., 2003; Lucarelli et al., 2014).

Partisol filters (PTFE, Whatman, pore size 1.0 µm) were divided into two equal portions and analysed for water-soluble ions and trace metals. The ionic components were extracted with distilled deionised water and analysed with ICS-2000 (anions) and Dionex DX 500 (cations) ion chromatography instruments. The full procedure for water-soluble ions analysis has been discussed in Yin et al. (2010). The second half PTFE filters were extracted with reverse aqua regia solution as described in Harrison et al. (2003). The extracts were assayed for relevant metals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500 Ce). Blank filters were run for all elemental analyses to correct for background levels of elements in the filters used; and also to determine detection limits of the analytes. PM$_{10}$, fine (PM$_{2.5}$), and coarse (PM$_{2.5-10}$) mass concentration data were obtained for daily samples by weighing.

2.2 Data Analysis

Data were subjected to statistical manipulations including descriptive, analysis of variance, and Duncan Multiple Range Test (DMRT) using SPSS for Windows version 19.0. Source identification and apportionment was carried out with the Multilinear Engine ME-2 receptor model (Paatero, 1999 and 2000).
2.2.1 Brief description of ME-2 model

ME-2 is a least squares program for solving multi-linear problems. Specifically, it solves models where the data values are fitted by sums of products of unknown factor elements (Paatero, 2000). For bilinear problems it takes the form \( X = G \cdot F + E \), where \( X \) is the known \( n \) by \( m \) matrix of the \( m \) measured chemical species in \( n \) samples; \( G \) is an \( n \) by \( p \) matrix of factor contributions to the samples; \( F \) is a \( p \) by \( m \) matrix of species concentrations in the factor profile. \( G \) and \( F \) are factor matrices to be determined and they are constrained to non-negative values only. \( E \) is defined as a residual matrix i.e. the difference between the measurement \( X \) and the model \( Y = G \cdot F \) as a function of \( G \) and \( F \).

One advantage in using ME-2 is that a priori information can be added as linear constraints in the object function to be minimized instead of using the generic rotational tools available in Positive Matrix Factorization (Paatero and Hopke, 2009; Amato et al., 2009; Amato and Hopke, 2012; and therein cited literature).

In this work, the datasets analysed with ME-2 comprised only normal variables, defined according to the signal-to-noise criterion reported in Paatero and Hopke (2003).

Uncertainties for Partisol daily samples were calculated using the formula adopted by Viana et al. (2008b) as \( 0.1 \cdot C + \text{MDL}/3 \); where \( C \) is the concentration and \( \text{MDL} \) is the method detection limit. All below-detection-limit data were treated equally by replacing with \( 1/2 \cdot \text{MDL} \) and their corresponding uncertainties calculated as \( 5/6 \cdot \text{MDL} \). Missing data were replaced with the geometric mean values and then down-weighed assigning them an uncertainty calculated as \( 4 \cdot C \), with \( C \) being the concentration value (Polissar et al., 1998). Streaker hourly data were pre-treated according to Polissar et al. (1998) as the below-detection limit data and experimental uncertainty (comprising...
counting statistics error, uncertainty on the measurement standard and spectra fitting errors) were available for each hourly entry. MDLs for daily and hourly data are reported in Table 1.

ME-2 analysis on the hourly data refers to the parallel sampling periods at LW and FS sites (i.e. about 300 hours in total), where the fine and the coarse PM fractions were summed up obtaining the PM$_{10}$ elemental dataset to be analysed with ME-2. In this work, the high-resolution dataset was exploited to retrieve a detailed identification of the different sources affecting PM$_{10}$ levels registered in the steelworks area, especially focusing on different iron-making and steel-making processes and aiming at improving the source apportionment with daily samples.

Partisol daily data collected at different sites in the steelworks area were pooled together in order to get a dataset suitable for multivariate analysis (N=99). This approach is supported by the similarity in the major sources impacting on the LW and FS sites as shown by the ME-2 analysis on the hourly data (see section 3.2). It is worth noting that sampling at the four sites occurred almost in parallel (i.e. during the same days) and the sampling stations were all around the steelworks area; thus, pooling all the data together might have helped in disentangling sources which at one single site would have been collinear. As a matter of fact, the average source apportionment is referred to the investigated area as a whole.

Following Amato and Hopke (2012), in this work two physical constraints deriving from mass conservation were incorporated in the analysis of daily data in order to improve the obtained solution for daily samples: 1) the single source contributions on a given day must be smaller than PM mass concentration on the same day; 2) for each source, the sum of factor profile must be less than unity.
3. RESULTS AND DISCUSSION

3.1 Elemental and Ion Concentrations for Daily PM Data

Table 2 shows the mean concentrations of mass, ionic and metal components from 29 days of Partisol data collected at the four monitoring sites, with their percentages in the total PM mass.

During the monitoring campaign PM$_{10}$ daily mass concentrations exceeded the 50 µg/m$^3$ limit value on only one occasion at the FS site. In total, secondary aerosol components (nss-SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) constituted 43% of measured PM$_{2.5}$ at FS, 30% at PS, 54% at DS and 67% at LW. Na$^+$ and Cl$^-$ were also significant components of PM$_{2.5}$ (7-14%) and especially of PM$_{2.5-10}$ (16-34%) at all monitoring sites. Among heavy metals, the most abundant in PM$_{2.5}$ were Fe and Zn at all sites and in PM$_{2.5-10}$ only Fe showed relevant contributions, i.e. ranging from 5 to 9%, with the highest percentages at FS and PS (i.e. the nearest to the blast furnace plant and to major roads). In both the fine and coarse PM fractions K$^+$, Mg$^{2+}$, Ca$^{2+}$, and Al contributed a few percent to PM mass.

The average wind rose registered during the investigated period is reported in Figure 2.

Meteorological data are calculated for the Margam station (next to the Fire Station site) belonging to the Automatic Urban and Rural Network by the Department for Environment, Food and Rural Affairs (DEFRA, http://uk-air.defra.gov.uk/data/).

3.2 Source Identification with Streaker Hourly Data

Direct information on the mass on Streaker samples is not available so that ME-2 results can be used for a detailed source identification (i.e. the factor profiles will be given in arbitrary units) but not for obtaining a complete source apportionment (D’Alessandro et al. 2003).

ME-2 analysis (base case) gave meaningful results for the 6-factor solution; it showed very good correlations ($R^2=0.80-0.99$) between measured and modelled elemental concentrations and elements.
were reconstructed within 20% (i.e. modelled to measured concentration ratio in the range 0.8-1) at both sites. Exceptions were Cu and Pb (and also Ti at LW). The Cu concentrations were fairly well reconstructed (i.e. in the worst case within 2% with $R^2=0.99$) considering the 7-factor solution where Cu appeared as a unique factor. On the contrary, Pb peaks were always poorly reconstructed also when considering a higher number of factors.

The 6-factor solution for PM$_{10}$ (i.e. fine + coarse PM fraction) collected at the Fire Station (main site) and Little Warren (coastal site) stations is reported in Figure 3. Chemical profiles (bars in arbitrary units) and explained variation values (EVF) are represented.

It is worth noting that in almost all cases the factors showed fairly similar profiles and EVF at both sites pointing to the same sources impacting on the areas adjacent to the steelworks. The major difference was found for the Steel 2 factor, as will be explained in the following.

Polar plots given in Figure 4 (LW site on the left and FS on the right) were also inspected for a more effective discrimination of different emission sources. Polar plots derive from the ME-2 analysis of the Streaker hourly data and show the wind direction (angle from centre) and wind speed (distance from centre) dependence of the resolved factors attributed to emission sources (Carslaw and Ropkins, 2012; Carslaw, 2013).

Blast furnaces (BF), sinter plant, basic oxygen steel-making (BOS) plant, coke-making plant, rolling mills, and ore stockyards are located in a southerly and westerly sector from the FS (170-270°) site at Port Talbot (see Figure 1). This is reflected in the directional pattern of all factors related to steelworks emissions reported in this work. From the LW site, the steel industry is located within the south and south-east sectors (100-180°). The majority of factors and especially those associated with steelworks emissions at the LW site show an association with this sector.
Factor 1 is labelled as “Marine Aerosol” according to the high EVF values and contributions of Cl, Na, and Mg, which are typical markers for sea salt (Viana et al., 2008a; and reference therein). As expected, the marine factor (Figure 4a) is strongly associated with westerly winds and its impact can be seen at both sites.

The high EVF values for Fe and Mn in factor 2 and the dominant Fe concentration in the chemical profile suggest apportionment to the iron-making plant (Dall’Osto et al., 2008; Mazzei et al., 2008) and especially to the blast furnace (BF) emissions; this factor is named “Steel 1 (BF)”. The removal of the S content in the pig iron-making process is facilitated by Mn and lime; the former can be in the iron mineral or is specifically inserted as auxiliary mineral. Lime is generally produced by limestone (CaCO₃) decomposition or alternatively it is introduced with the fluxing agent. The latter process can contribute to Ca found in the chemical profile of factor 2. The polar plots (Figure 4b) show that the Steel 1 contributions come from the BF area at both locations.

Factor 3 is named “Steel 2 (BOS)” due to the presence of Zn as the marker element (i.e. with the highest EVF value). Indeed, the use of galvanised scrap in the BOS has been stated to increase Zn concentrations in the steelworks processing section (Oravisjarvi et al., 2003; Hleis et al., 2013). This is the factor with the largest difference in the chemical profiles obtained at LW and FS as there is a not negligible contribution of S at LW and Fe at FS site; although their EVF values are of very little importance here. A likely S-rich source contribution at the LW site is from shipping emissions of sulphur dioxide on the adjacent waterway and in the in-shore and off-shore harbours (see Figure 1). Previous work has reported the accumulation of sulphate and nitrate on metal-rich particles (e.g. forming ZnSO₄ and PbSO₄ particles) as well as on sea salt or soil dust particles (e.g. forming Na₂SO₄ and NaNO₃ particles) (Sullivan et al., 2007; Marris et al., 2012; Perrone et al., 2013). The other relevant difference is the presence of Fe in the FS profile that could be due to a meteorological collinearity between the BOS and the BF plant. Further investigation on this Fe content is needed to
disentangle the contribution of these different sources. The polar plots (Figure 4c) are consistent
with the BOS location in respect to the measuring sites and show somehow a narrower directional
sector, pointing at the existence of pollution plumes from this plant.

In factor 4, sulphur is the dominant element in the profile at both sites. Also Cu and Pb at LW and
Pb at FS show EVF values larger than 0.3. The high S concentration can be related to coke making
emissions rich in SO₂; Pb and SO₂ were attributed to coking emissions also in previous work (e.g.
Pacyna, 1987; Pancras et al., 2013). The SO₂ emissions can promote sulphate aerosol formation as
well as the accumulation of sulphate on metals emitted by different iron and steel-making processes
as reported above. In addition to sources located in the steelworks area, the polar plots for this
factor (Figure 4d) at both sites show contributions coming from the east and the centre of the plots.
The EVF values of S, Cu, and Pb together with the polar plots for factor 4 suggest a possible
association with traffic emissions (Pant and Harrison, 2013; and references therein). Likely these
are non-exhaust and exhaust emissions due to both heavy duty traffic in the steelworks area, which
is estimated as 25,000 vehicle movements a day, and traffic on major roads due to the M4 and A48
located nearby (DfT, 2012). This factor is called “Steel 3 (coking) + Traffic”, where Steel 3
comprises primary and secondary (i.e. metals and sulphates) contributions from the coking plant.

Factor 5 is enriched in Na and S and shows EVF values higher than 0.3 for Na, Mg, Al at both sites
and additionally S at FS site. The polar plots for this factor (Figure 4e) point at a widespread source
with higher contributions coming from the south-west (and to a lesser extent from the east) at LW
and west (and to a lesser extent from the south-east) at FS. The spatial distribution and the chemical
profile of this factor suggest the association with “background aerosol” with a mixed marine (i.e.
aged aerosol) and mineral origin. Indeed, the Mg-to-Na ratio at both sites (0.12-0.14) is consistent
with the expected (0.12) seawater value (Seinfeld and Pandis, 1998). Moreover, Marris et al. (2012)
during near-field transport of industrial plumes attributed the presence of Na₂SO₄ and NaNO₃
particles to aged sea-salts due to the reaction of NaCl with gaseous anthropogenic pollutants like SO₂ and NOₓ producing a Cl loss. Mineral components like aluminosilicates, calcite, gypsum and metallic elements were also found by Marris et al. (2012) in binary mixtures with marine particles resulting from the mixing with dust of continental origin. In our study, re-suspended dust in the steelworks area could give the soil-related contribution and likely the hot-spots observed in the polar plots.

The factor 6 profile is characterised by the presence of Al, Si, and Ca at both sites. In Figure 3, EVF values larger than 0.3 for Al, Si, Ca, Ti at LW and Al, Si, Cu at FS can be seen. The polar plots (Figure 4f) show high contributions from the westerly, south-westerly and north-westerly directions at the FS site and from the west and south-east at LW thus pointing to different contributing sources. Investigations performed on stack emissions from sintering units (Marris et al., 2012; Setyan et al., 2013) report that emissions coming especially from the cooling area of the sintering plant largely consist of internally mixed aluminosilicates/metallic particles thus suggesting an association between factor 6 and sinter plant emissions (Steel 4). This is consistent with the sinter plant unit location (see Figure 1). Considering the factor profile and EVF values, a contribution due to slag processing cannot be excluded as Proctor et al. (2000) report that BF slag mainly consists of silica and alumina from the iron ore and Ca, Mg are primarily from the added flux. Sometimes slags are also used as road materials, landfill cover material, cement additive and other applications. At FS site there is also a high EVF for Cu (not observed at LW) that could be due to a very local road dust contribution as FS is next to major roads. Finally, the high concentration coming from the west at both sites can be an indication of a contribution by mineral elements re-suspended from the nearby sandy seashore. For sake of brevity, this factor is tentatively labelled as “Steel 4 (sintering) + Dust”.

12
In Figure 5 the temporal patterns of the factors resolved by ME-2 are represented in arbitrary units for the FS and LW sites. It is worth noting that the marine aerosol source shows a fair agreement in the temporal patterns at the two sites while the steelworks-related sources are characterised by sharp peaks occurring at different times at the two locations. The background aerosol source has a more irregular character likely due to the behaviour of re-suspended soil-related and aged marine aerosol in connection with different wind regimes. The temporal behaviours observed highlight the need for high resolution techniques when studying such a kind of emissions.

3.3 Source apportionment for Partisol Daily Data

Figures 6a-c show the chemical profiles and explained variation values obtained with ME-2 for Partisol daily PM$_{10}$, PM$_{2.5}$, and PM$_{2.5-10}$ data. Figures 7a-c show the corresponding average source apportionment for the steelworks area. It is worth noting that in this case the compositional data and mass concentrations from 4 different stations were pooled together. However, the analysis of the Streaker hourly data reported in the previous section indicated that there are no significant differences in the sources impacting in the steelworks area; therefore, the pooling of the compositional data can be performed in order to get a more robust source identification.

The optimal ME-2 solution showed 6 factors for PM$_{10}$ (in agreement with the sources resolved in the hourly datasets), 7 factors for PM$_{2.5}$, and 6 factors for PM$_{2.5-10}$. The $Q_{\text{main-to-}Q_{\text{teo}}}$ ratio was 1.5, 2, and 1.8 for PM$_{10}$, PM$_{2.5}$, and PM$_{2.5-10}$, respectively. This ratio between Q values is often used as an indicator for a good fit of the data (Belis et al., 2013). The computed versus measured PM$_{10}$ mass was higher than 0.95 in all cases showing a fairly good correlation ($R^2=0.92$ and 0.95 for PM$_{10}$ and PM$_{2.5-10}$; $R^2=0.73$ for PM$_{2.5}$). The factors related to iron- and steel-making emissions were labelled, as far as possible, with the same names given in the solution obtained for the hourly data.
The high EVF values for Na, Mg, and Cl and the profile in factor 1 for PM$_{10}$ (Figure 6a) point at the association with the “Marine aerosol” source. It seems specifically a fresh marine contribution as the Cl-to-Na ratio is 1.7 and the Mg-to-Na ratio is 0.10, in good agreement with the average composition of the sea salt (Seinfeld and Pandis, 1998). However, the profile is enriched in Fe, Ca, and Al which are likely due to a meteorological collinearity with the industrial emission sources; indeed, to reach the FS, DS, and PS sites the marine air masses overpass the steelworks area. In the average source apportionment (Figure 7a) this factor accounts for 28% of the PM$_{10}$ mass. The marine aerosol source is also present in the ME-2 solutions obtained for the fine and the coarse PM fractions separately (Figures 6b and 6c) accounting for 20% and 30%, respectively (Figures 7b and 7c). In the fine fraction the Cl-to-Na ratio is about 1.2 (vs. 2 in the coarse fraction) suggesting that aged marine aerosol is likely to be the contributor in the smallest PM fraction.

All PM fractions show high EVF values for Cu, Sb, and Ba in factor 2 for PM$_{10}$, which is labelled as “Traffic”. These trace metals are a signature of road traffic especially from brake wear (Sternbeck et al., 2002; Thorpe and Harrison, 2008; Pant and Harrison, 2013). It accounts for 16% of the PM$_{10}$ mass. The Cu/Sb ratio is 3.2 to be compared to 4.6 (± 2.3) proposed by Sternbeck et al. (2002) for brake wear particles. Considering ME-2 results presented in Figures 6b and 6c for the traffic factor, this ratio ranges from 2.3 in the fine PM fraction to 4.9 in the coarse PM fraction.

In factor 3, Fe and Mn show the highest EVF values in all PM fractions. Also Ca in PM$_{10}$ and Ni and Pb in PM$_{2.5-10}$ show EVF values higher than 0.3. Fe, Mn, and Ca are typical of blast furnace (BF) emissions as already discussed in the hourly data results and the factor is called “Steel 1”, accordingly. Fe has been generally observed at all the processing units of integrated steel production (Oravisjarvi et al., 2003; Machemer, 2004; Moreno et al., 2004; Connell et al., 2006; Tsai et al., 2007; Dall’Osto et al., 2008; Hleis et al., 2013). However, the recent source profile study of integrated steel facilities by Hleis et al. (2013) showed a more elevated Fe concentration from the
BF relative to other steelworks units. The average contribution of the Steel 1 source to PM$_{10}$ is 19% and it is by far the largest one among those related to the steelworks activities. Steel 1 contribution explains 9% and 28% of the fine and coarse PM mass, respectively.

For all PM fractions EVF values in factor 4 are dominated by Zn and Cd; in addition, Pb is present in this factor with its highest concentration when compared to other factors. Zn has been already mentioned as the marker element of BOS emissions and Pb was found in the corresponding profile obtained with the Streaker hourly dataset. The presence of K and Cl in the chemical profile of this factor for PM$_{10}$ and PM$_{2.5}$, known as major components in sinter plant emissions, together with the high EVF value for Cd point at the sinter plant unit as the most likely additional contributor (Oravisjarvi et al., 2003). Therefore, this factor is named “Steel 2 (BOS) + Steel 4 (sinter plant)”. It explains on average 3% of the PM$_{10}$ mass, 5% of the fine fraction mass and 3% of the PM coarse mass.

Factor 5 in PM$_{10}$ has similarities with factor 5 resolved in the hourly resolution data so that it is labelled accordingly as “background aerosol”. This source contributes 11% to PM$_{10}$ mass (6% in the fine fraction and 10% in the coarse PM).

Factor 6 for PM$_{10}$ is characterised by the relevant presence of sulphate, nitrate, and ammonium in the chemical profile with high EVF values thus relating it to secondary components of aerosol. In this factor the sulphate-to-ammonium ratio is 2.8 suggesting that sulphate is mainly in the form of ammonium sulphate; the nitrate in the profile is likely to be attributed to other chemical compounds (e.g. NaNO$_3$). Metals in the source profile suggest that a contribution coming from one of the production units in the steelworks area is superimposed. Coke-making is likely to be the emission source because of the concomitant presence of Pb and sulphate, similarly to what was found for the
hourly resolution results. This composite factor for PM$_{10}$ is labelled as “Secondary aerosol + Steel 3” and on average it accounts for about 22% of the PM$_{10}$ mass.

As mentioned before, for PM$_{2.5}$ the optimal ME-2 solution is the 7-factor one (Figure 6b), which separates the contributions from sulphates and nitrates accounting for 27% and 20%, respectively (Figure 7b). The sulphate-to-ammonium ratio is 2.2 in factor 6 and the nitrate-to-ammonium ratio is 4.6 in factor 7 indicating the possibility of having ammonium sulphate and nitrate in the fine PM fraction. Again, the presence of heavy metals in the profile of factor 6 –especially Pb – together with sulphates might be due to coking. In Figure 6b, factor 6 and factor 7 for PM$_{2.5}$ are called “Ammonium Sulphate + Steel 3” and “Ammonium Nitrate”, respectively.

In factor 6 for the PM$_{2.5-10}$ fraction (Figure 6c) nitrates and sulphates appear together with very high sulphate-to-ammonium and nitrate-to-ammonium ratios (i.e. 18 and 27, respectively) thus excluding the presence of ammonium nitrate and sulphate in the PM coarse fraction. This factor is named “Sulphates + Nitrates” and other chemical forms of sulphates and nitrates must be considered (as mentioned above in the text). Also in this case, the presence of metals in the profile is indicative of additional contributions coming from the steelworks primary emissions. This factor accounts for 13% of the coarse PM mass (Figure 7c).

4. CONCLUSIONS

The hourly data collected at Port Talbot captured the peculiarities of different emissions from the integrated iron and steel-making facility and were effective in resolving contributions from different steelworks units that the daily data could not always detect due to the short time characterising these emissions. Moreover, the hourly resolution demonstrated high metal concentrations lasting a few hours which may lead to an exposure problem in this area.
The receptor model analysis of daily and hourly data collected at Port Talbot has allowed identification of 6 factors for PM$_{10}$ and PM$_{2.5-10}$ and 7 factors for PM$_{2.5}$. The polar plots for the ME-2 profiles of the hourly data were helpful to resolve sources with similar chemical signatures. Additionally, the polar plots were able to identify the directional locations of different steel processing units resolved by ME-2. Contributions not clearly singled out using the hourly data alone (e.g. secondary contributions or traffic) are mainly ascribed to the lack of suitable markers; it is thus desirable in future work to combine hourly resolution data on different chemical components (e.g. more elements, ions, carbonaceous components). Overall the steelworks emissions assigned to blast furnaces (Steel 1), basic oxygen furnace steelmaking plant (Steel 2), and sinter unit (Steel 4) account for 23% of PM$_{10}$ mass. Other source contributions in the area are marine aerosol (28%), secondary aerosol and coking (Steel 3) (22%), traffic emissions (16%), and background aerosol (11%). The major contributor among the various steelwork units are the blast furnaces accounting for one-fifth of the PM$_{10}$ mass. It is interesting to note that large source contributions to the coarse PM fraction come from Steel 1 (BF) accounting on average for 28% of the measured mass concentration (vs. 9% in the fine fraction). As for PM$_{2.5}$, not surprisingly, the largest contribution is given by secondary components (i.e. ammonium sulphate and nitrate), which explain about half of the PM fine fraction mass.

By and large, both daily and hourly ME-2 profiles are complementary and effective in identifying and apportioning pollution sources. The chemical profiles for both daily and hourly data have been able to separate contributions from different steelworks units, which have not been previously reported in any published literature known to us.

5. ACKNOWLEDGEMENTS

We are grateful for support from the National Centre for Atmospheric Science (NCAS) which is funded by the UK Natural Environment Research Council and for support to Adewale Taiwo from...
the Tertiary Education Trust Fund (TETFund), Federal University of Agriculture, Abeokuta, Nigeria. Furthermore, we would like to formally thank Neath-Port Talbot Council, the Environment Agency Wales, Mid and West Wales Fire and Rescue Service, Dwr Cymru and Dyffryn School, Port Talbot for hosting our measurements.
REFERENCES


Amato F, Hopke PK. Source apportionment of the ambient PM2.5 across St. Louis using constrained positive matrix factorization. Atmos Environ 2012;46:329-337.


Carslaw DC. The Openair manual — open-source tools for analysing air pollution data. Manual for version 0.8-0, King’s College London, 2013.


Harrison RM, Jones AM, Lawrence RG. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmos Environ 37;2003:4927-4933.


Moreno T, Jones TP, Richards RJ. Characterisation of aerosol particulate matter from urban and industrial environments: examples from Cardiff and Port Talbot, South Wales, UK. Sci Total Environ 2004;334-335:337-346.

Oravisjarvi K, Timonen,KL, Wiikinkoski T, Ruuskanen AR, Heinanen K., Ruuskanene J. Source contributions to PM$_{2.5}$ particles in the urban air of a town situated close to a steel works. Atmos Environ 2003;37:1013-1022.

Paatero P. The multilinear engine - a table-driven least squared program for solving multilinear problems, including the n-way parallel factor analysis model. University of Helsinki, Department of Physics, 1999.


Pant P, Harrison RM. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. Atmos Environ 2013;77:78-97.

Passant NR, Peirce M, Rudd HJ, Scott DW, Marlowe I, Watterson JD. UK Particulate and Heavy Metal Emissions from Industrial Processes. A report produced for the Department for Environment, Food & Rural Affairs, the National Assembly for Wales, the Scottish Executive and the Department of the Environment in Northern Ireland. AEAT-6270 Issue 2, 2002.


Pope CA, Dockery DW. Health effects of fine particulate air pollution: Lines that connect. JAWMA 2006;56:709-742.


TABLE LEGENDS

Table 1: Minimum Detection Limits (MDL) for daily and hourly data.

Table 2: Mean, standard deviation and percentage composition of water soluble ion and metal concentrations of daily PM$_{2.5}$ and PM$_{2.5-10}$ concentrations in Port Talbot.

FIGURE LEGENDS

Figure 1: Map of study area

Figure 2: Average wind rose for Margam station (Fire Station site) in Port Talbot during the campaign period

Figure 3: 6-Factor solution resolved by ME-2 for hourly PM$_{10}$ (i.e. fine + coarse PM fraction) collected at Little Warren (on the left) and Fire Station (on the right). Chemical profiles are represented as bars (in arbitrary units) and the explained variation values (EVF) as dots.

Figure 4: Bi-variate polar plots of hourly data in ME-2 factor contributions. (a) Marine aerosol; (b) Steel 1; (c) Steel 2; (d) Secondary + Traffic; (e) Background aerosol; (f) Steel 4 + Dust. LW site on the left; FS on the right.

Figure 5: Hourly temporal patterns of factor contributions obtained in the ME-2 6-factor solution.

Figure 6a: 6-Factor solution resolved by ME-2 for PM$_{10}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.

Figure 6b: 7-Factor solution resolved by ME-2 for PM$_{2.5}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.

Figure 6c: 6-Factor solution resolved by ME-2 for PM$_{2.5-10}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.

Figure 7a: Source apportionment for PM$_{10}$ (daily data) in the steelworks area.

Figure 7b: Source apportionment for PM$_{2.5}$ (daily data) in the steelworks area.

Figure 7c: Source apportionment for PM$_{2.5-10}$ (daily data) in the steelworks area.
Table 1: Minimum Detection Limits (MDL) for daily and hourly data.

<table>
<thead>
<tr>
<th>Species</th>
<th>Daily samples (Partisol)</th>
<th>Hourly samples (Streaker)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM$_{2.5}$ (ng m$^{-3}$)</td>
<td>PM$_{2.5}$ (ng m$^{-3}$)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>42</td>
<td>31</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>34</td>
<td>26</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>127</td>
<td>101</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>33</td>
<td>26</td>
</tr>
<tr>
<td>K$^+$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>32</td>
<td>26</td>
</tr>
<tr>
<td>Al</td>
<td>30.3</td>
<td>8.05</td>
</tr>
<tr>
<td>V</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>1.46</td>
<td>0.39</td>
</tr>
<tr>
<td>Mn</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>2.62</td>
<td>0.70</td>
</tr>
<tr>
<td>Ni</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>Zn</td>
<td>1.31</td>
<td>0.35</td>
</tr>
<tr>
<td>Cd</td>
<td>0.02</td>
<td>0.004</td>
</tr>
<tr>
<td>Sb</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Ba</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>Pb</td>
<td>0.16</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Mean, standard deviation and percentage composition of water soluble ion and metal concentrations of Partisol daily data (PM$_{2.5}$ and PM$_{2.5-10}$) in Port Talbot.

<table>
<thead>
<tr>
<th>Site</th>
<th>Fire Station (N=29)</th>
<th>Prince Street (N=12)</th>
<th>Dyffryn School (N=29)</th>
<th>Little Warren (N=29)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM$_{2.5}$ (µg/m$^3$)</td>
<td>PM$_{2.5-10}$ (µg/m$^3$)</td>
<td>PM$_{2.5}$ (µg/m$^3$)</td>
<td>PM$_{2.5-10}$ (µg/m$^3$)</td>
</tr>
<tr>
<td></td>
<td>Mean ±SD</td>
<td>Mean ±SD</td>
<td>Mean ±SD</td>
<td>Mean ±SD</td>
</tr>
<tr>
<td>Cl</td>
<td>7.4 ± 1.1</td>
<td>13.6 ± 0.7</td>
<td>9.2 ± 1.7</td>
<td>16.7 ± 0.5</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.4 ± 0.3</td>
<td>1.3 ± 0.6</td>
<td>0.4 ± 0.6</td>
<td>1.8 ± 0.7</td>
</tr>
<tr>
<td>nss-SO$_4^{2-}$</td>
<td>0.6 ± 0.4</td>
<td>0.8 ± 0.4</td>
<td>0.5 ± 0.3</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>ss-SO$_4^{2-}$</td>
<td>0.09 ± 0.1</td>
<td>0.21 ± 0.3</td>
<td>0.08 ± 0.2</td>
<td>0.27 ± 0.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.34 ± 0.2</td>
<td>0.82 ± 0.3</td>
<td>0.31 ± 0.2</td>
<td>1.06 ± 0.6</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.68 ± 0.9</td>
<td>0.07 ± 0.1</td>
<td>0.58 ± 0.6</td>
<td>0.06 ± 0.1</td>
</tr>
<tr>
<td>K</td>
<td>0.01 ± 0.07</td>
<td>0.13 ± 0.1</td>
<td>0.03 ± 0.1</td>
<td>0.16 ± 0.1</td>
</tr>
<tr>
<td>Mg</td>
<td>0.05 ± 0.07</td>
<td>0.13 ± 0.1</td>
<td>0.03 ± 0.1</td>
<td>0.12 ± 0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>0.15 ± 0.13</td>
<td>0.80 ± 1.0</td>
<td>0.11 ± 0.1</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Al*</td>
<td>128.9 ± 142.6</td>
<td>109.6 ± 140.8</td>
<td>110.6 ± 120.6</td>
<td>117.9 ± 120.6</td>
</tr>
<tr>
<td>V*</td>
<td>±3.4 ± 58.5</td>
<td>±7.9 ± 44.8</td>
<td>±16.1 ± 34.1</td>
<td>±4.1 ± 13.8</td>
</tr>
<tr>
<td>Cr*</td>
<td>±5.2 ± &lt;1</td>
<td>±5.0 ± &lt;1</td>
<td>±0.5 ± &lt;1</td>
<td>±0.4 ± &lt;1</td>
</tr>
<tr>
<td>Mn*</td>
<td>±15.2 ± 15.2</td>
<td>±12.7 ± 31.2</td>
<td>±7.5 ± 25.2</td>
<td>±7.3 ± 25.2</td>
</tr>
<tr>
<td>Fe*</td>
<td>±7.6 ± 35.1</td>
<td>±7.9 ± 44.8</td>
<td>±16.1 ± 34.1</td>
<td>±4.1 ± 13.8</td>
</tr>
<tr>
<td>Ni*</td>
<td>±173.9 ± 194.5</td>
<td>±290.3 ± 1439</td>
<td>±142.2 ± 421</td>
<td>±4.8 ± 12.5</td>
</tr>
<tr>
<td>Cu*</td>
<td>±0.20 ± &lt;1</td>
<td>±0.16 ± &lt;1</td>
<td>±0.12 ± &lt;1</td>
<td>±0.17 ± &lt;1</td>
</tr>
<tr>
<td>Zn*</td>
<td>±1.19 ± 2.05</td>
<td>±1.51 ± 1.69</td>
<td>±1.42 ± 1.45</td>
<td>±1.38 ± 1.12</td>
</tr>
<tr>
<td>Cd*</td>
<td>±1.21 ± 0.87</td>
<td>±1.75 ± 0.5</td>
<td>±1.42 ± 0.31</td>
<td>±1.38 ± 1.12</td>
</tr>
<tr>
<td>Sb*</td>
<td>±1.40 ± 3.03</td>
<td>±1.69 ± 1.4</td>
<td>±1.90 ± 2.01</td>
<td>±1.90 ± 2.01</td>
</tr>
<tr>
<td>Ba*</td>
<td>±1.42 ± 2.04</td>
<td>±1.95 ± 1.42</td>
<td>±1.38 ± 1.12</td>
<td>±1.38 ± 1.12</td>
</tr>
<tr>
<td>Pb*</td>
<td>±3.88 ± 4.0</td>
<td>±7.98 ± 4.2</td>
<td>±9.27 ± 5.1</td>
<td>±16.86 ± 4.13</td>
</tr>
</tbody>
</table>

Superscripts of the same letter on the rows are not significantly different at p<0.05, * units in ng/m$^3$

nss-SO$_4^{2-}$ calculated following Sciare et al. (2003)
Figure 1: Map of study area.
Figure 2: Average wind rose for Margam station (Fire Station site) in Port Talbot during the campaign period.
Figure 3: 6-Factor solution resolved by ME-2 for hourly PM10 (i.e. fine + coarse PM fraction) collected at Little Warren (on the left) and Fire Station (on the right). Chemical profiles are represented as bars (in arbitrary units) and the explained variation values (EVF) as dots.
Figure 4: Bi-variate polar plots of hourly data in ME-2 factor contributions. (a) Marine aerosol; (b) Steel 1; (c) Steel 2; (d) Secondary + Traffic; (e) Background aerosol; (f) Steel 4 + Dust. LW site on the left; FS on the right.
Figure 5: Hourly temporal patterns of factor contributions obtained in the ME-2 6-factor solution.
Figure 6a: 6-Factor solution resolved by ME-2 for PM$_{10}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.
Figure 6b: 7-Factor solution resolved by ME-2 for PM$_{2.5}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.
**Figure 6c:** 6-Factor solution resolved by ME-2 for PM$_{2.5-10}$ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.
Figure 7a: Source apportionment for PM$_{10}$ (daily data) in the steelworks area.

Figure 7b: Source apportionment for PM$_{2.5}$ (daily data) in the steelworks area.

Figure 7c: Source apportionment for PM$_{2.5-10}$ (daily data) in the steelworks area.