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Receptor Modelling of Airborne Particulate Matter in the Vicinity of a Major Steelworks Site

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31

32 **HIGHLIGHTS**

- 33 ➤ Air sampling has taken place at 4 sites around the steelworks.
- 34 ➤ Hourly and daily samples were collected with Streaker and Partisol samplers.
- 35 ➤ ME-2 was applied to both datasets for source apportionment.
- 36 ➤ PM contributions from individual steelworks processes are identified.
- 37 ➤ Steelworks emissions account for 45% of measured PM₁₀ mass.

38

39 **ABSTRACT**

40 In this study, the Multilinear Engine (ME-2) receptor model was applied to speciated particulate
41 matter concentration data collected with two different measuring instruments upwind and
42 downwind of a steelworks complex in Port Talbot, South Wales, United Kingdom. Hourly and daily
43 PM samples were collected with Streaker and Partisol samplers, respectively, during a one month
44 sampling campaign between April 18 and May 16, 2012. Daily samples (PM_{10} , $PM_{2.5}$, $PM_{2.5-10}$)
45 were analysed for trace metals and water-soluble ions using standard procedures. Hourly samples
46 ($PM_{2.5}$ and $PM_{2.5-10}$) were assayed for 22 elements by Particle Induced X-ray Emission (PIXE).
47 PM_{10} data analysis using ME-2 resolved 6 factors from both datasets identifying different steel
48 processing units including emissions from the blast furnaces (BF), the basic oxygen furnace
49 steelmaking plant (BOS), the coke-making plant, and the sinter plant. Steelworks emissions were
50 the main contributors to PM_{10} accounting for 45% of the mass when including also secondary
51 aerosol. The blast furnaces were the largest emitter of primary PM_{10} in the study area, explaining
52 about one-fifth of the mass. Other source contributions to PM_{10} were from marine aerosol (28%),
53 traffic (16%), and background aerosol (11%). ME-2 analysis was also performed on daily $PM_{2.5}$ and
54 $PM_{2.5-10}$ data resolving 7 and 6 factors, respectively. The largest contributions to $PM_{2.5-10}$ were from
55 marine aerosol (30%) and blast furnace emissions (28%). Secondary components explained one-
56 half of $PM_{2.5}$ mass. The influence of steelworks sources on ambient particulate matter at Port Talbot
57 was distinguishable for several separate processing sections within the steelworks in all PM
58 fractions.

59 **Keywords:** Steelworks; source apportionment; ME-2; hourly resolution; receptor modelling

60

61 **1. INTRODUCTION**

62 Both acute and chronic exposures to airborne particulate matter (PM) have been associated with
63 adverse effects upon health including premature mortality (Pope and Dockery, 2006).
64 Consequently, the World Health Organisation (WHO, 2006) recommends strict guidelines for
65 airborne particulate matter measured both as PM₁₀ and PM_{2.5}. Governments around the world are
66 developing and applying abatement strategies to reduce population exposures to particulate matter.
67 The development of cost-effective strategies depends critically upon a quantitative knowledge of
68 the contribution of different sources to airborne particulate matter concentrations. Receptor
69 modelling is a widespread approach to identify emission sources and to resolve their contribution to
70 PM mass (Viana et al., 2008a).

71
72 For many years the town of Port Talbot has suffered some of the worst air quality in the United
73 Kingdom (AQEG, 2011). The basic operational steelworks units in Port Talbot are coke making,
74 sintering, blast furnace, basic oxygen furnace and other steel processing units (Passant et al., 2002).
75 Earlier work (Moreno et al., 2004; Dall'Osto et al., 2008; Hayes and Chatterton, 2009) has
76 identified the steelworks as a major contributor to local PM₁₀ concentrations and the steelworks
77 units have been recognised as major emission sources of heavy metals such as chromium, copper,
78 lead, cadmium, arsenic, zinc, manganese, iron, nickel, vanadium and selenium (Passant et al., 2002;
79 Moreno et al., 2004; Dall'Osto et al., 2008). However, knowledge has been lacking as to the
80 magnitude of the contribution of the steelworks to airborne PM concentrations as well as the
81 identity of the predominant sources within the steelworks.

82
83 The present study focuses on the identification and apportionment of emission sources of particulate
84 matter pollution in the vicinity of the integrated steelworks complex located in Port Talbot.
85 As a complement to previous studies, which used approaches including scanning electron
86 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.

113 **2.1 Sampling and Analysis**

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

116 Streaker samples (collected on Nuclepore filters for PM_{2.5} and Kapton foils for PM_{2.5-10}) were
117 analysed by Particle Induced X-ray Emission (PIXE) at the 3 MV Tandetron accelerator facility of
118 the INFN-LABEC laboratory in Florence, Italy. Twenty-two elements from sodium to lead were
119 analysed in both fine and coarse Streaker PM samples. Details of the Streaker sampler and PIXE
120 analysis have been extensively reported elsewhere (D'Alessandro et al., 2003; Lucarelli et al.,
121 2014).

122 Partisol filters (PTFE, Whatman, pore size 1.0 µm) were divided into two equal portions and
123 analysed for water-soluble ions and trace metals. The ionic components were extracted with
124 distilled deionised water and analysed with ICS-2000 (anions) and Dionex DX 500 (cations) ion
125 chromatography instruments. The full procedure for water-soluble ions analysis has been discussed
126 in Yin et al. (2010). The second half PTFE filters were extracted with reverse aqua regia solution as
127 described in Harrison et al. (2003). The extracts were assayed for relevant metals by Inductively
128 Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500 Ce). Blank filters were run for all
129 elemental analyses to correct for background levels of elements in the filters used; and also to
130 determine detection limits of the analytes. PM₁₀, fine (PM_{2.5}), and coarse (PM_{2.5-10}) mass
131 concentration data were obtained for daily samples by weighing.

133

134 **2.2 Data Analysis**

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

139 2.2.1 *Brief description of ME-2 model*

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

148
149 One advantage in using ME-2 is that a priori information can be added as linear constraints in the
150 object function to be minimized instead of using the generic rotational tools available in Positive
151 Matrix Factorization (Paatero and Hopke, 2009; Amato et al., 2009; Amato and Hopke, 2012; and
152 therein cited literature).

153
154 In this work, the datasets analysed with ME-2 comprised only normal variables, defined according
155 to the signal-to-noise criterion reported in Paatero and Hopke (2003).

156
157 Uncertainties for Partisol daily samples were calculated using the formula adopted by Viana et al.
158 (2008b) as $0.1 \cdot C + MDL/3$; where C is the concentration and MDL is the method detection limit. All
159 below-detection-limit data were treated equally by replacing with $1/2 \cdot MDL$ and their corresponding
160 uncertainties calculated as $5/6 \cdot MDL$. Missing data were replaced with the geometric mean values
161 and then down-weighted assigning them an uncertainty calculated as $4 \cdot C$, with C being the
162 concentration value (Polissar et al., 1998). Streaker hourly data were pre-treated according to
163 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 PM₁₀ 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 PM₁₀ 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.

190 3. RESULTS AND DISCUSSION

191 3.1 Elemental and Ion Concentrations for Daily PM Data

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

194

195 During the monitoring campaign PM_{10} daily mass concentrations exceeded the $50 \mu g/m^3$ limit value
196 on only one occasion at the FS site. In total, secondary aerosol components ($nss-SO_4^{2-}$, NO_3^- and
197 NH_4^+) constituted 43% of measured $PM_{2.5}$ at FS, 30% at PS, 54% at DS and 67% at LW. Na^+ and
198 Cl^- were also significant components of $PM_{2.5}$ (7-14%) and especially of $PM_{2.5-10}$ (16-34%) at all
199 monitoring sites. Among heavy metals, the most abundant in $PM_{2.5}$ were Fe and Zn at all sites and
200 in $PM_{2.5-10}$ only Fe showed relevant contributions, i.e. ranging from 5 to 9%, with the highest
201 percentages at FS and PS (i.e. the nearest to the blast furnace plant and to major roads). In both the
202 fine and coarse PM fractions K^+ , Mg^{2+} , Ca^{2+} , and Al contributed a few percent to PM mass.

203

204 The average wind rose registered during the investigated period is reported in Figure 2.
205 Meteorological data are calculated for the Margam station (next to the Fire Station site) belonging
206 to the Automatic Urban and Rural Network by the Department for Environment, Food and Rural
207 Affairs (DEFRA, <http://uk-air.defra.gov.uk/data/>).

208

209 3.2 Source Identification with Streaker Hourly Data

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

213

214 ME-2 analysis (base case) gave meaningful results for the 6-factor solution; it showed very good
215 correlations ($R^2=0.80-0.99$) between measured and modelled elemental concentrations and elements

216 were reconstructed within 20% (i.e. modelled to measured concentration ratio in the range 0.8-1) at
217 both sites. Exceptions were Cu and Pb (and also Ti at LW). The Cu concentrations were fairly well
218 reconstructed (i.e. in the worst case within 2% with $R^2=0.99$) considering the 7-factor solution
219 where Cu appeared as a unique factor. On the contrary, Pb peaks were always poorly reconstructed
220 also when considering a higher number of factors.

221

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

225

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

229

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

235

236 Blast furnaces (BF), sinter plant, basic oxygen steel-making (BOS) plant, coke-making plant,
237 rolling mills, and ore stockyards are located in a southerly and westerly sector from the FS (170-
238 270°) site at Port Talbot (see Figure 1). This is reflected in the directional pattern of all factors
239 related to steelworks emissions reported in this work. From the LW site, the steel industry is located
240 within the south and south-east sectors (100-180°). The majority of factors and especially those
241 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 (CaCO_3) 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 ZnSO_4 and PbSO_4 particles) as well as on sea salt or soil dust particles (e.g. forming Na_2SO_4 and NaNO_3 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

268 disentangle the contribution of these different sources. The polar plots (Figure 4c) are consistent
 269 with the BOS location in respect to the measuring sites and show somehow a narrower directional
 270 sector, pointing at the existence of pollution plumes from this plant.
 271

272 In factor 4, sulphur is the dominant element in the profile at both sites. Also Cu and Pb at LW and
 273 Pb at FS show EVF values larger than 0.3. The high S concentration can be related to coke making
 274 emissions rich in SO₂; Pb and SO₂ were attributed to coking emissions also in previous work (e.g.
 275 Pacyna, 1987; Pancras et al., 2013). The SO₂ emissions can promote sulphate aerosol formation as
 276 well as the accumulation of sulphate on metals emitted by different iron and steel-making processes
 277 as reported above. In addition to sources located in the steelworks area, the polar plots for this
 278 factor (Figure 4d) at both sites show contributions coming from the east and the centre of the plots.
 279 The EVF values of S, Cu, and Pb together with the polar plots for factor 4 suggest a possible
 280 association with traffic emissions (Pant and Harrison, 2013; and references therein). Likely these
 281 are non-exhaust and exhaust emissions due to both heavy duty traffic in the steelworks area, which
 282 is estimated as 25,000 vehicle movements a day, and traffic on major roads due to the M4 and A48
 283 located nearby (DfT, 2012). This factor is called “Steel 3 (coking) + Traffic”, where Steel 3
 284 comprises primary and secondary (i.e. metals and sulphates) contributions from the coking plant.
 285

286 Factor 5 is enriched in Na and S and shows EVF values higher than 0.3 for Na, Mg, Al at both sites
 287 and additionally S at FS site. The polar plots for this factor (Figure 4e) point at a widespread source
 288 with higher contributions coming from the south-west (and to a lesser extent from the east) at LW
 289 and west (and to a lesser extent from the south-east) at FS. The spatial distribution and the chemical
 290 profile of this factor suggest the association with “background aerosol” with a mixed marine (i.e.
 291 aged aerosol) and mineral origin. Indeed, the Mg-to-Na ratio at both sites (0.12-0.14) is consistent
 292 with the expected (0.12) seawater value (Seinfeld and Pandis, 1998). Moreover, Marris et al. (2012)
 293 during near-field transport of industrial plumes attributed the presence of Na₂SO₄ and NaNO₃

294 particles to aged sea-salts due to the reaction of NaCl with gaseous anthropogenic pollutants like
295 SO₂ and NO_x producing a Cl loss. Mineral components like aluminosilicates, calcite, gypsum and
296 metallic elements were also found by Marris et al. (2012) in binary mixtures with marine particles
297 resulting from the mixing with dust of continental origin. In our study, re-suspended dust in the
298 steelworks area could give the soil-related contribution and likely the hot-spots observed in the
299 polar plots.

300

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

318

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

326

327 **3.3 Source apportionment for Partisol Daily Data**

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

335

336 The optimal ME-2 solution showed 6 factors for PM_{10} (in agreement with the sources resolved in
337 the hourly datasets), 7 factors for $PM_{2.5}$, and 6 factors for $PM_{2.5-10}$. The Q_{main} -to- Q_{teo} ratio was 1.5,
338 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
339 an indicator for a good fit of the data (Belis et al., 2013). The computed versus measured PM_{10} mass
340 was higher than 0.95 in all cases showing a fairly good correlation ($R^2=0.92$ and 0.95 for PM_{10} and
341 $PM_{2.5-10}$; $R^2=0.73$ for $PM_{2.5}$). The factors related to iron- and steel-making emissions were labelled,
342 as far as possible, with the same names given in the solution obtained for the hourly data.

343

344 The high EVF values for Na, Mg, and Cl and the profile in factor 1 for PM₁₀ (Figure 6a) point at the
345 association with the “Marine aerosol” source. It seems specifically a fresh marine contribution as
346 the Cl-to-Na ratio is 1.7 and the Mg-to-Na ratio is 0.10, in good agreement with the average
347 composition of the sea salt (Seinfeld and Pandis, 1998). However, the profile is enriched in Fe, Ca,
348 and Al which are likely due to a meteorological collinearity with the industrial emission sources;
349 indeed, to reach the FS, DS, and PS sites the marine air masses overpass the steelworks area. In the
350 average source apportionment (Figure 7a) this factor accounts for 28% of the PM₁₀ mass. The
351 marine aerosol source is also present in the ME-2 solutions obtained for the fine and the coarse PM
352 fractions separately (Figures 6b and 6c) accounting for 20% and 30%, respectively (Figures 7b and
353 7c). In the fine fraction the Cl-to-Na ratio is about 1.2 (vs. 2 in the coarse fraction) suggesting that
354 aged marine aerosol is likely to be the contributor in the smallest PM fraction.

355

356 All PM fractions show high EVF values for Cu, Sb, and Ba in factor 2 for PM₁₀, which is labelled
357 as “Traffic”. These trace metals are a signature of road traffic especially from brake wear
358 (Sternbeck et al., 2002; Thorpe and Harrison, 2008; Pant and Harrison, 2013). It accounts for 16%
359 of the PM₁₀ mass. The Cu/Sb ratio is 3.2 to be compared to 4.6 (± 2.3) proposed by Sternbeck et al.
360 (2002) for brake wear particles. Considering ME-2 results presented in Figures 6b and 6c for the
361 traffic factor, this ratio ranges from 2.3 in the fine PM fraction to 4.9 in the coarse PM fraction.

362

363 In factor 3, Fe and Mn show the highest EVF values in all PM fractions. Also Ca in PM₁₀ and Ni
364 and Pb in PM_{2.5-10} show EVF values higher than 0.3. Fe, Mn, and Ca are typical of blast furnace
365 (BF) emissions as already discussed in the hourly data results and the factor is called “Steel 1”,
366 accordingly. Fe has been generally observed at all the processing units of integrated steel
367 production (Oravisjarvi et al., 2003; Machemer, 2004; Moreno et al., 2004; Connell et al., 2006;
368 Tsai et al., 2007; Dall’Osto et al., 2008; Hleis et al., 2013). However, the recent source profile study
369 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.

421 The receptor model analysis of daily and hourly data collected at Port Talbot has allowed
422 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-
423 2 profiles of the hourly data were helpful to resolve sources with similar chemical signatures.
424 Additionally, the polar plots were able to identify the directional locations of different steel
425 processing units resolved by ME-2. Contributions not clearly singled out using the hourly data
426 alone (e.g. secondary contributions or traffic) are mainly ascribed to the lack of suitable markers; it
427 is thus desirable in future work to combine hourly resolution data on different chemical components
428 (e.g. more elements, ions, carbonaceous components). Overall the steelworks emissions assigned to
429 blast furnaces (Steel 1), basic oxygen furnace steelmaking plant (Steel 2), and sinter unit (Steel 4)
430 account for 23% of PM_{10} mass. Other source contributions in the area are marine aerosol (28%),
431 secondary aerosol and coking (Steel 3) (22%), traffic emissions (16%), and background aerosol
432 (11%). The major contributor among the various steelwork units are the blast furnaces accounting
433 for one-fifth of the PM_{10} mass. It is interesting to note that large source contributions to the coarse
434 PM fraction come from Steel 1 (BF) accounting on average for 28% of the measured mass
435 concentration (vs. 9% in the fine fraction). As for $PM_{2.5}$, not surprisingly, the largest contribution is
436 given by secondary components (i.e. ammonium sulphate and nitrate), which explain about half of
437 the PM fine fraction mass.

438

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

443

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572

573 **TABLE LEGENDS**

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

575

576 **Table 2:** Mean, standard deviation and percentage composition of water soluble ion and metal
577 concentrations of daily PM_{2.5} and PM_{2.5-10} concentrations in Port Talbot.

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582 **FIGURE LEGENDS**

583

584 **Figure 1:** Map of study area

585

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

588 **Figure 3:** 6-Factor solution resolved by ME-2 for hourly PM₁₀ (i.e. fine + coarse PM fraction)
589 collected at Little Warren (on the left) and Fire Station (on the right). Chemical
590 profiles are represented as bars (in arbitrary units) and the explained variation values
591 (EVF) as dots.

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

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

597 **Figure 6a:** 6-Factor solution resolved by ME-2 for PM₁₀ (daily data) in the steelworks area.
598 Chemical profiles are represented as bars (in ng/ng) and the explained variation as
599 dots.

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

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

606 **Figure 7a:** Source apportionment for PM₁₀ (daily data) in the steelworks area.

607 **Figure 7b:** Source apportionment for PM_{2.5} (daily data) in the steelworks area.

608 **Figure 7c:** Source apportionment for PM_{2.5-10} (daily data) in the steelworks area.

609

610 **Table 1:** Minimum Detection Limits (MDL) for daily and hourly data.
611

Daily samples (Partisol)			Hourly samples (Streaker)		
Species	PM _{2.5} (ng m ⁻³)	PM _{2.5-10} (ng m ⁻³)	Species	PM _{2.5} (ng m ⁻³)	PM _{2.5-10} (ng m ⁻³)
Cl ⁻	42	31	Na	42	25
NO ₃ ⁻	34	26	Mg	22	13
SO ₄ ²⁻	200	150	Al	17	10
Na ⁺	127	101	Si	14	10
NH ₄ ⁺	33	26	S	15	12
K ⁺	2	2	Cl	17	12
Mg ²⁺	7	6	K	18	13
Ca ²⁺	32	26	Ca	13	9
Al	30.3	8.05	Ti	5	3
V	0.11	0.03	V	3	2
Cr	1.46	0.39	Cr	2	1
Mn	0.06	0.02	Mn	1	1
Fe	2.62	0.70	Fe	1	1
Ni	0.08	0.02	Ni	1	1
Cu	0.18	0.05	Cu	1	1
Zn	1.31	0.35	Zn	1	1
Cd	0.02	0.004	As	1	1
Sb	0.03	0.01	Se	1	1
Ba	0.10	0.03	Br	1	1
Pb	0.16	0.04	Rb	2	3
			Sr	2	3
			Pb	2	1

612

613

614 **Table 2:** Mean, standard deviation and percentage composition of water soluble ion and metal
615 concentrations of Partisol daily data (PM_{2.5} and PM_{2.5-10}) in Port Talbot.
616

Site	Fire Station (N=29)				Prince Street (N=12)				Dyffryn School (N=29)				Little Warren (N=29)			
Parameters	PM _{2.5} (µg/m ³)		PM _{2.5-10} (µg/m ³)		PM _{2.5} (µg/m ³)		PM _{2.5-10} (µg/m ³)		PM _{2.5} (µg/m ³)		PM _{2.5-10} (µg/m ³)		PM _{2.5} (µg/m ³)		PM _{2.5-10} (µg/m ³)	
	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%	Mean ±SD	%
Mass	7.4 ^a ±2.1	100	13.6 ^{bc} ±11.7	100	9.2 ^b ±1.7	100	16.7 ^c ±10.5	100	7.3 ^a ±3.0	100	8.3 ^a ±4.9	100	6.5 ^a ±2.5	10	9.3 ^{ab} ±4.36	100
Cl ⁻	0.34 ^a ±0.33	5	1.33 ^a ±1.06	10	0.41 ^a ±0.43	4	1.80 ^a ±1.34	11	0.44 ^a ±0.42	6	1.52 ^a ±1.54	20	0.40 ^a ±0.37	6	1.96 ^a ±1.47	21
NO ₃ ⁻	0.62 ^a ±0.49	8	0.45 ^a ±0.27	3	0.52 ^a ±0.41	6	0.47 ^a ±0.35	3	0.95 ^a ±0.81	13	1.03 ^b ±1.58	15	0.95 ^a ±0.74	15	0.81 ^{ab} ±0.79	9
nss-SO ₄ ²⁻	1.91 ^{ab} ±1.02	26	0.36 ^a ±0.38	3	1.66 ^a ±0.38	18	0.28 ^{ab} ±0.26	2	2.29 ^{ab} ±1.31	31	0.70 ^c ±0.46	9	2.51 ^b ±1.23	39	0.57 ^{bc} ±0.42	6
ss-SO ₄ ²⁻	0.09 ^a ±0.05	1	0.21 ^a ±0.13	2	0.08 ^a ±0.05	1	0.27 ^{ab} ±0.16	2	0.09 ^a ±0.05	1	0.21 ^{ab} ±0.15	3	0.12 ^b ±0.05	2	0.31 ^b ±0.19	3
Na ⁺	0.34 ^a ±0.20	5	0.82 ^a ±0.52	6	0.31 ^a ±0.19	3	1.06 ^{ab} ±0.62	6	0.34 ^a ±0.21	5	0.87 ^{ab} ±0.59	10	0.49 ^b ±0.22	8	1.23 ^b ±0.74	13
NH ₄ ⁺	0.68 ^a ±0.53	9	0.07 ^a ±0.06	<1	0.58 ^a ±0.34	6	0.06 ^a ±0.04	<1	0.75 ^a ±0.65	10	0.07 ^a ±0.09	2	0.82 ^a ±0.65	13	0.14 ^b ±0.11	2
K ⁺	0.11 ^a ±0.01	2	0.08 ^a ±0.07	1	0.14 ^a ±0.09	2	0.09 ^a ±0.08	1	0.10 ^a ±0.07	1	0.08 ^a ±0.06	1	0.15 ^a ±0.10	2	0.12 ^a ±0.07	1
Mg ²⁺	0.05 ^a ±0.04	1	0.13 ^a ±0.10	1	0.05 ^a ±0.02	1	0.16 ^a ±0.11	1	0.04 ^a ±0.03	1	0.12 ^a ±0.09	1	0.06 ^a ±0.03	1	0.15 ^a ±0.09	2
Ca ²⁺	0.15 ^a ±0.13	2	0.80 ^b ±0.77	6	0.11 ^a ±0.07	1	0.91 ^b ±0.77	5	0.10 ^a ±0.15	1	0.41 ^a ±0.45	5	0.15 ^a ±0.17	2	0.45 ^a ±0.37	5
Al*	128.9 ^b ±34.3	2	142.6 ^b ±58.5	1	109.6 ^a ±7.9	1	140.8 ^{ab} ±44.8	1	116.0 ^{ab} ±16.1	2	110.6 ^a ±34.1	1	117.9 ^{ab} ±24.7	2	123.6 ^{ab} ±48.3	1
V*	0.52 ^a ±0.23	<1	0.53 ^{bc} ±0.42	<1	0.50 ^a ±0.23	<1	0.64 ^c ±0.34	<1	0.49 ^a ±0.21	<1	0.41 ^a ±0.32	<1	0.59 ^a ±0.28	<1	0.31 ^{ab} ±0.18	<1
Cr*	3.48 ^a ±1.52	<1	2.89 ^a ±1.52	<1	4.76 ^a ±2.04	<1	3.67 ^a ±1.16	<1	2.78 ^a ±1.55	<1	3.14 ^a ±1.49	<1	4.52 ^a ±3.19	<1	2.97 ^a ±1.49	<1
Mn*	5.72 ^a ±7.6	<1	26.47 ^{bc} ±35.1	<1	12.76 ^b ±11.8	<1	29.52 ^c ±27.0	<1	7.03 ^a ±10.7	<1	12.65 ^{ab} ±13.8	<1	3.84 ^a ±4.8	<1	10.0 ^a ±12.5	<1
Fe*	173 ^a ±237	2	1196 ^b ±1642	9	290 ^b ±229	3	1439 ^b ±1485	9	142 ^a ±147	2	421 ^a ±433	5	104 ^a ±108	2	520 ^a ±669	6
Ni*	0.20 ^a ±0.33	<1	0.19 ^{ab} ±0.22	<1	0.16 ^a ±0.27	<1	0.24 ^b ±0.22	<1	0.12 ^a ±0.17	<1	0.11 ^a ±0.15	<1	0.12 ^a ±0.20	<1	0.14 ^{ab} ±0.22	<1
Cu*	1.89 ^a ±1.21	<1	2.05 ^b ±0.87	<1	2.90 ^b ±1.51	<1	3.20 ^c ±1.69	<1	1.42 ^a ±0.90	<1	1.45 ^{ab} ±1.0	<1	1.38 ^a ±1.26	<1	1.12 ^a ±0.70	<1
Zn*	43.0 ^a ±85.55	1	7.30 ^a ±8.03	<1	67.97 ^a ±165.8	1	16.26 ^a ±30.87	<1	71.51 ^a ±117.2	1	20.31 ^a ±26.48	<1	33.98 ^a ±86.7	1	8.30 ^a ±17.71	<1
Cd*	0.26 ^a ±0.55	<1	0.02 ^a ±0.06	<1	0.88 ^a ±2.11	<1	0.06 ^a ±0.12	<1	0.69 ^a ±1.34	<1	0.08 ^a ±0.15	<1	0.31 ^a ±0.52	<1	0.03 ^a ±0.09	<1
Sb*	0.57 ^a ±0.52	<1	0.36 ^b ±0.21	<1	0.99 ^b ±1.14	<1	0.66 ^c ±0.34	<1	0.38 ^a ±0.32	<1	0.13 ^a ±0.14	<1	0.53 ^a ±0.71	<1	0.11 ^a ±0.22	<1
Ba*	1.04 ^b ±0.5	<1	3.03 ^b ±2.06	<1	1.69 ^c ±0.75	<1	4.04 ^c ±2.32	<1	0.49 ^a ±0.25	<1	1.41 ^a ±0.81	<1	0.34 ^a ±0.26	<1	1.15 ^a ±0.70	<1
Pb*	4.42 ^a ±3.88	<1	2.04 ^{ab} ±2.40	<1	7.65 ^a ±7.98	<1	2.95 ^b ±4.20	<1	8.12 ^a ±9.27	<1	1.44 ^a ±1.51	<1	7.02 ^a ±6.86	<1	1.32 ^a ±1.43	<1

617 Superscripts of the same letter on the rows are not significantly different at p<0.05, * units in ng/m³
618 nss-SO₄²⁻ calculated following Sciare et al. (2003)
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623 **Figure 1:** Map of study area.

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

632 **Figure 3:** 6-Factor solution resolved by ME-2 for hourly PM10 (i.e. fine + coarse PM fraction)
633 collected at Little Warren (on the left) and Fire Station (on the right). Chemical profiles are
634 represented as bars (in arbitrary units) and the explained variation values (EVF) as dots.

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(4a)

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(4b)

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(4c)

(4d)

(4e)

(4f)

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 PM₁₀ (daily data) in the steelworks area. Chemical profiles are represented as bars (in ng/ng) and the explained variation as dots.

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

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

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743 **Figure 7a:** Source apportionment for PM₁₀ (daily data) in the steelworks area.

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746 **Figure 7b:** Source apportionment for PM_{2.5} (daily data) in the steelworks area.

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748 **Figure 7c:** Source apportionment for PM_{2.5-10} (daily data) in the steelworks area.