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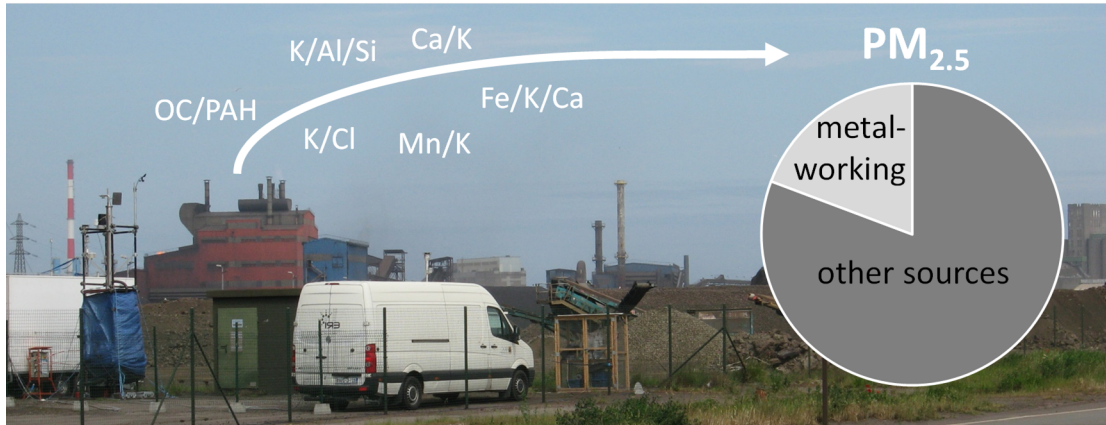
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CRedit statement

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Characterization and source apportionment of single particles from metalworking activities

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35 Abstract

36 Industrial metalworking facilities emit a variety of air toxics including volatile organic
37 compounds, polycyclic aromatic hydrocarbons (PAHs) and heavy metals. In order to investigate
38 these emissions, a 1-month multi-instrument field campaign was undertaken at an industrial site
39 in Grande-Synthe, Dunkirk (France), in May and June 2012. One of the main objectives of the
40 study was to provide new information on the chemical composition of particulate matter with
41 aerodynamic diameters smaller than 2.5 μm ($\text{PM}_{2.5}$) in the vicinity of metalworking facilities. An
42 aerosol time-of-flight mass spectrometer (ATOFMS) was deployed to provide size-resolved
43 chemical mixing state measurements of ambient single particles at high temporal resolution. This
44 mixing state information was then used to apportion $\text{PM}_{2.5}$ to local metalworking facilities
45 influencing the receptor site. Periods when the site was influenced by metalworking sources were
46 characterised by a pronounced increase in particles containing toxic metals (manganese, iron,
47 lead) and polycyclic aromatic hydrocarbons (PAHs) with a variety of chemical mixing states.
48 The association of specific particle classes with a nearby ferromanganese alloy manufacturing
49 plant was confirmed through comparison with previous analysis of raw materials (ores) and
50 chimney filter particle samples collected at the facility. Particles associated with emissions from
51 a nearby steelworks were also identified. The contribution of local metalworking activities to
52 $\text{PM}_{2.5}$ at the receptor site for the period when the ATOFMS was deployed ranged from 1-65%
53 with an average contribution of 17%, while the remaining mass was attributed to other local and
54 regional sources. These findings demonstrate the impact of metalworking facilities on air quality
55 downwind and provide useful single particle signatures for future source apportionment studies
56 in communities impacted by metalworking emissions.

57

58 **Keywords:**

59 Particulate matter; source apportionment; mass spectrometry; industrial emissions;
60 metalworking; air quality

61

62

63

64 1 Introduction

65 Negative health outcomes, lower crop yields, building damage and other impacts associated with
66 industrial air pollution and greenhouse gas emissions were estimated to cost Europe over €300
67 billion between 2008 and 2012 (European Environment Agency, 2014). Almost a third of
68 emissions of particulate matter with aerodynamic diameters smaller than 10 μm (PM_{10}) in France
69 (CITEPA, 2014) are attributed to industrial sources. The city of Dunkirk lies in the Hauts de
70 France region of Northern France and is home to over 200 industrial facilities from many sectors
71 including refining and cement production. Dunkirk also contains one of Europe's largest
72 steelworks, which emits approximately 3,000 t of PM per year (Flament et al., 2008). Numerous
73 local industrial facilities generate plumes that impact air quality in the surrounding areas
74 depending on local meteorological conditions, and local PM_{10} concentrations regularly exceed
75 the European threshold value (24-hour average of $50 \mu\text{g m}^{-3}$) (Setyan et al., 2019).

76 The physico-chemical nature of industrial PM varies considerably, particularly in terms of
77 composition, depending on the type of industrial processes involved (Sanderson et al., 2014;
78 Taiwo et al., 2014; Riffault et al., 2015). Ambient concentrations of particulate phase metals tend
79 to be greater at locations directly influenced by industrial activities than at rural or urban
80 locations (Osornio-Vargas Alvaro et al., 2003; Schaumann et al., 2004; Lim et al., 2010;
81 Mohiuddin et al., 2014). Heavy metals and polycyclic aromatic hydrocarbons (PAHs) are
82 important contributors to particle toxicity (Harrison and Yin, 2000). The generation of reactive
83 oxygen species (ROS) and the development of asthma and cardiopulmonary disease have been
84 linked to exposure to metals (Schaumann et al., 2004; Majestic et al., 2007). $\text{PM}_{2.5}$ collected
85 from the same industrial area of Dunkirk investigated in this work has been recently
86 demonstrated to damage DNA through an *in vitro* assessment of immortalized lung cells (Platel
87 et al., 2020). Thus, the impact of industrial emissions on downwind air quality needs to be
88 assessed in order to better understand human exposure to the associated air toxics.

89 Particulate PAH and metal content studies have been performed in the Dunkirk area previously
90 due to the importance of metalworking sources and their proximity to large residential areas
91 (Ledoux et al., 2006; Ledoux et al., 2009; Flament et al., 2008; Alleman et al., 2010; Marris et
92 al., 2012; Marris et al., 2013; Hleis et al., 2013; Mbengue et al., 2014; Cazier et al., 2016; Crenn
93 et al., 2018). In terms of source apportionment, the tracers used have included elemental ratios,

94 for examples Mn/Fe as a signature for a ferromanganese alloy metalworking facility, V/Ni for
95 petrochemical facilities and isotopes of Pb and Fe as a signature for a local steelworks (Veron et
96 al., 1999; Ledoux et al., 2006; Flament et al., 2008; Ledoux et al., 2009; Alleman et al., 2010;
97 Marris et al., 2012). Emissions from the steelworks are also the dominant source of air emissions
98 of Fe in Dunkirk, and the facility is estimated to emit 620 t of Fe annually (Flament et al., 2008).
99 Anthropogenic particulate Fe emissions are of additional concern because of their higher
100 solubility relative to Fe present in naturally occurring dust. Thus anthropogenic particulate Fe is
101 more bioavailable than natural Fe dust, and the former can modulate primary productivity in
102 high-nutrient, low chlorophyll (HNLC) ocean regions (Ito and Shi, 2016). Anthropogenic
103 sources are responsible for approximately 7% of the 8.4 Mt of Fe deposited to oceans annually,
104 and therefore have significant impacts upon carbon dioxide fixation globally (Wang et al., 2015).

105 The density and diversity of sources and emission profiles in Dunkirk complicates source
106 apportionment efforts based on off-line analysis significantly (Alleman et al., 2010). One
107 technique that is well suited to providing information on the size-resolved chemical composition
108 and mixing state of particles emitted by industrial activities is single particle mass spectrometry.
109 A review of industrial studies utilising this technique can be found in Riffault et al. (2015). The
110 capability to provide mixing state information for individual particles is key to the role single
111 particle mass spectrometry plays in source apportionment. Ambient particles containing specific
112 internal mixtures of metals and other primary organic and inorganic species have been
113 successfully assigned to their respective sources using this technique. For example, internally
114 mixed Pb/Zn/Cl particles have been assigned to industrial waste incineration (Moffet et al.,
115 2008b), Ga- and Se-containing particles particles have been associated with coal-fired power
116 generation (Pekney et al., 2006; Snyder et al., 2009) and internally mixed V/Ni/sulfate particles
117 have been associated with ship exhaust (Ault et al., 2009; Healy et al., 2009). Fe, Zn and Pb-
118 containing particles have also been previously assigned to steelwork facility operations
119 (Dall'Osto et al., 2008).

120 In this context, the NANO-INDUS field campaign was performed in the multi-industry
121 influenced zone of Grande-Synthe in Dunkirk, France, close to a ferromanganese alloy facility
122 and a steelworks (Setyan et al., 2019). An aerosol time-of-flight mass spectrometer (ATOFMS)
123 was deployed to provide size-resolved chemical composition and mixing state data for industrial
124 PM_{2.5} with high temporal resolution. The ATOFMS data were used in combination with support

125 instrumentation measurements to apportion PM_{2.5} to local and regional sources and to assess the
126 impact of local metalworking facilities on air quality at the receptor site. Comparison of the
127 ambient ATOFMS data with previous analysis of raw materials (ores) and particles collected on
128 industrial filters from the ferromanganese alloy facility's chimneys (Arndt et al., 2016), enabled
129 more effective source assignments for the particle classes observed during the field campaign.

130 **2 Experimental**

131 **2.1 Sampling site and Instrumentation**

132 All measurements were made in the industrial area of Grande-Synthe, Dunkirk (51.028809 N,
133 2.269448 E, 10 m above sea level), approximately 800 m southwest of a ferromanganese alloy
134 manufacturing facility and 1 km southwest of a major steelworks (Figure S1). The adjacency of
135 these two sources precludes separation of their air pollutant contributions based on wind
136 direction alone (Setyan et al., 2019). Other nearby sources include a petrochemical storage
137 facility <500 m to the west of the site and urban centres located to the east of the site (Fort-
138 Mardyck and Dunkirk town centre, ~2 km and ~ 7 km from the site, respectively). The field
139 campaign was undertaken from 15 May 2012 to 12 June 2012. An overview of the campaign,
140 local meteorology, the instrumentation deployed and broad PM composition is described in
141 detail elsewhere (Setyan et al., 2019). Date and time are reported in Coordinated Universal Time
142 (UTC). PM_{2.5} mass concentrations were determined every 2 hours with a MP101M Beta Gauge
143 monitor. 24 to 48-hour filter samples were also collected on 25mm polycarbonate membrane
144 filters (WhatmanTM) using 13- and 3-stage cascade impactors, and weighed with a micro-
145 balance (UMT2, Mettler Toledo, Switzerland) (Mbengue et al., 2014, 2017).

146 The ATOFMS (TSI model 3800) was operated continuously from 18th May – 8th June 2012. A
147 detailed description of the ATOFMS can be found elsewhere (Gard et al., 1997). Briefly, it
148 consists of (i) an aerodynamic focusing lens (TSI AFL100) (Su et al., 2004) used to optimize
149 particle transmission in the aerodynamic diameter (d_a) range 100-3000 nm, (ii) a particle sizing
150 region, and (iii) a bipolar reflectron time-of-flight mass spectrometer. Single particles are
151 desorbed/ionised using a pulsed Nd:YAG laser ($\lambda = 266$ nm, ~1 mJ pulse⁻¹) and positive and
152 negative ion mass spectra of individual aerosol particles are simultaneously collected for
153 successfully ionised particles. ATOFMS particle counts are scaled to account for sizing and other
154 instrument biases as discussed below.

155

156 2.2 ATOFMS Data Analysis

157 Mass spectral data for over 800,000 single particles was collected using the ATOFMS during the
158 deployment period and was clustered using the *K*-means algorithm ($K=80$), as described
159 elsewhere (Gross et al., 2010; Healy et al., 2010; Healy et al., 2013). Clusters with similar mass
160 spectral profiles, size distributions and temporality were combined. The final merged clusters
161 were then identified as particle “classes”; 33 in total. Approximately 15% of the particles ionised
162 did not produce positive ion mass spectra. The absence of positive ions is likely a result of
163 desorption/ionization matrix effects and precludes the assignment of these particles to a specific
164 category due to the absence of useful marker ions.

165 The particle class nomenclature used here is regularly used in the literature (Dall'Osto and
166 Harrison, 2006; Spencer et al., 2006; Ault et al., 2010; Pratt and Prather, 2012) and typically
167 denotes the dominant species in the positive ion mass spectra. For example, a particle class with
168 high intensities for sodium and elemental carbon is labelled Na-EC. In some cases this is
169 followed by secondary species detected in the negative ion mass spectra (e.g. EC-NH₄-NO₃),
170 referring to elemental carbon internally mixed with ammonium and nitrate.

171 The ATOFMS does not measure particle number or mass concentrations quantitatively, but
172 instead provides particle counts classified by aerodynamic diameter. The size-dependent
173 transmission efficiency of the focusing lens, data acquisition "busy time", and limited detection
174 of particles <150 nm complicate accurate counting of particles over the ATOFMS size range
175 (100-3000 nm d_a). The desorption/ionization laser used by the ATOFMS also complicates
176 quantitative speciation efforts. Differences in laser output power and variations in power density
177 across the laser beam between pulses (Steele et al., 2005; Wenzel and Prather, 2004) alter the
178 mass of each particle that is effectively desorbed impacting mass spectral signal intensities
179 (Gross et al., 2000a; Reinard and Johnston, 2008).

180 Thus the measured ATOFMS counts were scaled using two quantitative particle counting
181 instruments operated concurrently; an optical particle counter (OPC, TSI model 3300) and a
182 scanning mobility particle sizer (SMPS, TSI DMA model 3080 and CPC model 3010). Scaling
183 the ATOFMS number concentration data requires conversion of d_a (aerodynamic diameter) into
184 the corresponding volume equivalent diameter (d_{ve}), using the following relationship:

$$d_a = \frac{\rho_p d_{ve}}{\rho_0 \chi} \quad (1)$$

186 where ρ_p is the particle density, assumed for the purposes of number-size distribution scaling to
 187 be 1.7 g cm^{-3} as per previous applications of the method (Morawska et al., 1999; Reinard et al.,
 188 2007), d_{ve} is the volume equivalent diameter (operationally equivalent to electrical mobility
 189 diameter d_m measured by the SMPS and optical diameter d_o measured by the OPC), ρ_0 is
 190 standard density (1 g cm^{-3}) and χ represents the dynamic shape factor (e.g. 1, representing
 191 spherical shape). This is a simplified version of particle property relationships that are covered in
 192 detail elsewhere (DeCarlo et al., 2004). Mass concentrations can then be calculated from the
 193 scaled number concentrations as follows (Reinard et al., 2007):

$$m = \frac{\pi}{6} \rho_p d_{ve}^3 \quad (2)$$

195 The accuracy of the conversion of number concentrations to mass concentrations is dependent on
 196 the representativeness of χ and ρ_p for each type of particle. In the absence of morphology data χ
 197 is assumed to be 1. The use of a single density value, ρ_p , for conversion of ATOFMS scaled
 198 particle number concentrations to mass concentrations has previously resulted in good agreement
 199 with other quantitative measurements (Qin et al., 2006; Healy et al., 2013; Zhou et al., 2016).
 200 However, this simplification is not entirely accurate because different particle types exhibit
 201 different densities depending upon their chemical composition (Spencer and Prather, 2006;
 202 Reinard et al., 2007). A range of more representative densities, estimated from the bulk densities
 203 of the chemical components observed in the mass spectra (Bein et al., 2006; Reinard et al.,
 204 2007), was therefore used to convert the scaled number-size distributions to mass concentrations
 205 for each particle class, as listed in Table S1. ATOFMS-derived mass concentrations for $\text{PM}_{2.5}$
 206 were averaged to hourly and 24 to 48-hour time resolutions for comparison with $\text{PM}_{2.5}$ measured
 207 concurrently on-line using the beta gauge instrument and off-line through gravimetric filter
 208 analysis, respectively. Similar ATOFMS-based source apportionment techniques have been
 209 performed previously to separate local and regional contributions to ambient PM in Paris, France
 210 and the apportionment results were found to agree well with those modelled using a regional
 211 chemical transport model (Healy et al., 2013; Skyllakou et al., 2014).

212 **3 Results and Discussion**

213 **3.1 ATOFMS Results Overview**

214 ATOFMS-derived mass concentrations of $PM_{2.5}$ were in reasonable temporal agreement with
215 concurrently measured on-line beta gauge $PM_{2.5}$ mass concentrations at 2-hour resolution ($R^2 =$
216 0.62) and in good temporal agreement with gravimetric $PM_{2.5}$ mass concentrations at 24 to 48-
217 hour resolution ($R^2 = 0.91$) as shown in Figure 1. This temporal agreement is in line with
218 previous studies involving similar scaling procedures for single particle mass spectrometers (R^2
219 = 0.64-0.91) (Qin et al., 2006; Jeong et al., 2011; Healy et al., 2013; Zhou et al., 2016) and
220 indicates that changes in ATOFMS-derived mass concentrations are representative of variations
221 in ambient $PM_{2.5}$ mass concentrations at the site during the field study.

222 The 33 distinct ATOFMS particle classes identified through clustering were grouped into ten
223 general “categories” for simplicity based on the dominant elements in their respective mass
224 spectra. Briefly, the categories identified are: K-rich, EC-rich (elemental carbon), Na-rich, Fe-
225 rich, Ca-rich, V-rich, Mn-rich, OC-rich (organic carbon), Pb-rich/Li-rich and Others. The
226 relative contributions of each category in terms of mass concentration is shown in Table S1. The
227 dominant categories are K-rich (24%), EC-rich (23%) Na-rich (10%) and Fe-rich (10%),
228 followed by OC-rich (4%), Ca-rich (4%), V-rich (4%), Mn-rich (3%) and Pb-rich/Li-rich (3%).
229 The “Others” category contains particle classes with minimal mass contributions (Sulfur and
230 Amines, <1%). Temporal trends for each category are shown in Figure 2. It is clear from these
231 temporal trends that the Na-rich, K-rich and EC categories exhibit prolonged, persistent mass
232 contributions, consistent with regional background sources. Briefly, the K-rich category is
233 dominated by a single particle class (K- NO_3) often associated with regional biomass combustion
234 (Silva et al., 1999), routinely observed in regional background air in ATOFMS datasets collected
235 across Europe (Dall'Osto et al., 2009; Healy et al., 2015; Arndt et al., 2017). The ATOFMS is
236 highly sensitive to potassium (Gross et al., 2000a), and while the potassium ion is a dominant
237 feature of biomass burning particle mass spectra, it is typically present as a trace component,
238 with EC, OC and secondary inorganics dominating the composition in terms of mass (Healy et
239 al., 2013). Particles in the EC-rich category are associated with various combustion sources,
240 including vehicle exhaust and biomass burning (Spencer et al., 2006; Moffet et al., 2008a), and
241 are often observed to be internally mixed with OC and secondary inorganics (Cahill et al., 2012;
242 Healy et al., 2012). The Na-rich category is predominantly comprised of supermicron sea salt
243 internally mixed with nitrate, which is expected for a coastal urban site (Gard et al., 1998). These
244 three major particle categories are routinely observed in ATOFMS field studies. However,

245 several of the less abundant particle classes were found to be associated with local metalworking
246 activities.

247 As outlined by Setyan et al. (2019), two distinct meteorological sea-breeze periods when winds
248 were predominantly from the northeast were identified during the NANO-INDUS field campaign
249 when the sampling site was downwind of the nearby ferromanganese and steelworks facilities
250 (May 25-28 and June 02-03). During these events, particle number concentrations increased
251 considerably, with concurrent increases in non-refractory chloride, organic aerosol and metals
252 including manganese and iron. As shown in Figure 2, concentrations of several metal-rich
253 particle categories detected by the ATOFMS were enhanced during these periods (shaded in
254 grey). Particle classes associated with the ferromanganese alloy facility were identified through
255 comparison with previous scanning electron microscopy/electron dispersive X-ray spectrometry
256 (SEM-EDX) and ATOFMS analysis of raw materials (ores) and cooling, firing and smelting
257 chimney filter samples previously collected at the facility (Arndt et al., 2016). Particle classes
258 were assigned to the steelworks based on previous off-line elemental analysis of particles
259 collected downwind of this facility (Mbengue et al., 2017) and previous ATOFMS measurements
260 made in the vicinity of a large steelworks in the UK (Dall'Osto et al., 2008; Dall'Osto et al.,
261 2012).

262 **3.2 Metalworking Particle Source Identification**

263 Temporal trends for individual particle classes exhibiting elevated concentrations during the
264 prolonged periods when the site was downwind of the ferromanganese facility and the
265 steelworks (Setyan et al., 2019) are shown in Figure 2. These include metal-rich particles with a
266 variety of chemical mixing states and particles containing OC and polycyclic aromatic
267 hydrocarbons (PAHs).

268 **Mn-rich particles:**

269 Three distinct Mn-containing particle classes were identified. Mn-K particles were characterized
270 by the presence of Mn^+ (m/z 55) and K^+ (m/z 39) while Mn-Al-K particles exhibited a strong
271 additional signal for aluminium (Al^+ , m/z 27) and Mn-K-Fe particles exhibited a strong
272 additional signal for iron (Fe^+ , m/z 56) Average mass spectra for the three Mn-containing classes
273 are shown in Figure 3, and the positive ion mass spectra are consistent with ATOFMS positive

274 ion mass spectra for particles collected at the ferromanganese facility (Arndt et al., 2016) (Figure
275 S2). Mn-K particles are consistent with samples of the ores used at the facility as well as filter
276 samples from the cooling chimney. Mn-Al-K particles also resemble both ore samples and the
277 filter samples from the chimneys. Finally, Mn-K-Fe particle mass spectra are consistent with
278 mass spectra for ore samples exclusively. Ambient Mn-K, Mn-Al-K and Mn-K-Fe are all
279 enriched in nitrate ($\text{NO}_2^-/\text{NO}_3^-$, m/z -46/-62) and chloride (Cl^- , m/z -35) relative to the facility
280 samples (Arndt et al., 2016), likely due to secondary accumulation of inorganic ions either
281 through mixing with either inorganic gases from the metalworking facilities themselves or with
282 ambient air after emission. All three Mn-rich particle classes are therefore assigned to the
283 ferromanganese facility, which has been previously identified as the major local source of Mn in
284 a previous apportionment study based on off-line filter analysis (Alleman et al., 2010).

285 **Fe-rich particles:**

286 Mass spectra for particles containing internally mixed iron, potassium and calcium (Fe-K-Ca)
287 feature a dominant signal for Fe^+ (m/z 56) followed by K^+ (m/z 39), Ca^+ (m/z 40), Na^+ (m/z 23)
288 and Al^+ (m/z 27) (Figure 4). Negative ion mass spectra contain peaks corresponding to chloride
289 (Cl^- , m/z -35) and nitrate ($\text{NO}_2^-/\text{NO}_3^-$, m/z -46/-62). Fe-K-Na particles are quite similar to Fe-K-
290 Ca particles, differing only in the intensities of sodium and potassium relative to iron. The mass
291 spectral features of both particle classes are similar to internally mixed Fe/K/Ca particles
292 collected from the chimneys of the ferromanganese facility (Arndt et al., 2016) (Figure S3),
293 although the ambient particles shown in Figure 4 exhibit higher signals for nitrate ($\text{NO}_2^-/\text{NO}_3^-$,
294 m/z -46/-62), again indicating uptake of nitrate after emission. While similarities exist between
295 ambient and ferromanganese facility sample mass spectra for Fe-containing particles, the nearby
296 steelworks remains the largest source of particulate iron in Dunkirk. A previous analysis of the
297 steelworks particulate emissions demonstrated that most particles emitted were comprised of
298 either Fe_2O_3 , CaCO_3 , KCl or were graphite flakes (Flament et al., 2008). Iron-rich particles
299 similar to the ATOFMS Fe-K-Ca and Fe-K-Na classes were also detected by ATOFMS near a
300 steelworks in Port Talbot (UK) (Dall'Osto et al., 2008), where they accounted for 3% of the
301 particles detected and were attributed to the hot and cold mills. In the absence of any unique ions
302 to differentiate between iron-containing particles from the steelworks and those emitted by the
303 ferromanganese facility, and given that Fe/K/Ca particles only contributed a small fraction of the
304 particles identified in the ferromanganese facility samples (Arndt et al., 2016), it is likely that the

305 majority of iron-containing particles detected during the field study originated from the
306 steelworks. Setyan et al (2019) found that Mn/Fe elemental ratios in filter samples collected
307 during the periods when the receptor site was downwind of the metalworking facilities were
308 between the ratios expected for emissions from the ferromanganese facility and the steelworks,
309 suggesting that emissions from both facilities were impacting the site. Contributions of Fe from
310 both facilities were also observed in the previous source apportionment study (Alleman et al.,
311 2010).

312 **K-rich particles:**

313 As shown in Figure 5, K-Cl particles are characterized by peaks for K^+ (m/z 39), Na^+ (m/z 23),
314 Cl^- (m/z -35), and nitrate (NO_2^-/NO_3^- , m/z -46/-62). The local steelworks emits potassium
315 chloride during the sintering process (Setyan et al., 2019), and potassium chloride emissions are
316 estimated to represent ~40% of total sintering emissions from the facility (Flament et al., 2008;
317 Hleis et al., 2013). K-Cl particles were not observed in the chimney filter or ore samples from the
318 ferromanganese facility (Arndt et al., 2016). K-Cl particles have however, been detected
319 downwind of the Port Talbot steelworks (Dall'Osto et al., 2008) and are thus assigned to the
320 steelworks here. K-Al-Si particles are characterized by signals for K^+ (m/z 39), Na^+ (m/z 23), Fe^+
321 (m/z 56), AlO^- (m/z -43), $AlO(OH)^-/SiO_2^-/CO_3^-$ (m/z -60), SiO_3^- (m/z -76), $AlSiO_3^-$ (m/z -103),
322 nitrate (NO_2^-/NO_3^- , m/z -46/-62), phosphate (PO_3^- , m/z -79), and chloride (Cl^- , m/z -35/-37)
323 (Figure 5). No aluminium signal was observed in K-Al-Si positive mass spectra, likely due to
324 matrix-related ion suppression (Reinard and Johnston, 2008). K-Cl and K-Al-Si particles were
325 not observed in the ferromanganese facility samples and are therefore assigned to the steelworks.
326 However, K-Al particles were positively identified in the ferromanganese facility firing chimney
327 samples (Figure S4). Ambient K-Al particles produced stronger signals for nitrate (NO_2^-/NO_3^- ,
328 m/z -46/-62) and sulfate (HSO_4^- , m/z -97) but both the ambient and the firing chimney K-Al
329 particles exhibited similar signals for F^- (m/z -19). Therefore fluoride represents a useful
330 discriminatory marker for identifying potassium-containing particles from the ferromanganese
331 facility.

332 **Ca-rich particles:**

333 Ca particles are characterized by a strong signal for Ca^+ (m/z 40) and smaller signals for Na^+ (m/z
334 23) and CaO^+ (m/z 56), while Ca-K particles contain stronger signals for Na^+ (m/z 23) and K^+
335 (m/z 39) as shown in Figure 6. Based on comparison with the ferromanganese facility samples,
336 both Ca and Ca-K particles appear to originate from the firing chimney, although ambient Ca-K
337 particles exhibit higher signals for Na than the chimney samples (Figure S3). Negative ion mass
338 spectra for both ambient Ca and Ca-K particles also exhibited higher signals for nitrate (NO_2^-
339 $/\text{NO}_3^-$, m/z -46/-62) and sulfate (HSO_4^- , m/z -97) than their respective chimney sample particles
340 again likely due to secondary accumulation after emission. A signal for fluoride is present in the
341 ambient Ca negative ion mass spectra (F^- , m/z -19), consistent with the firing chimney samples,
342 however this ion is absent in the ambient Ca-K particle spectra, indicating that ambient Ca-K
343 particles may be associated with the steelworks instead. Flament et al. (2008) noted that calcium
344 salts, including calcite and lime, are used in the sintering process at the steelworks, however the
345 Ca-containing particles produced in that case are aggregates of Fe_2O_3 , CaCO_3 and KCl . Ca-
346 containing particles constituted only 8% of the particles analyzed from the steelworks sintering
347 process by Flament et al. (2008), while Ca-rich particles accounted for approximately 80% of
348 the particles in the firing chimney filter sample (Arndt et al., 2016). Ca-containing particles have
349 also been assigned to the blast furnace unit of the Port Talbot steelworks (Taiwo et al., 2014), but
350 those particles were also internally mixed with OC, and no Ca particles were reported in the
351 previous Port Talbot steelworks studies by Dall'Osto et al. (2008,2012). Thus, while there
352 remains a possibility that some of the Ca-rich particles could have originated from the
353 steelworks, the ferromanganese facility is likely the dominant source.

354 **OC-rich particles:**

355 Three OC-containing particle classes were identified, of which the OC class was the dominant
356 contributor in terms of mass. Average mass spectra are shown in Figure 7. All three classes are
357 characterized by the presence of hydrocarbon fragments in the positive mass spectra
358 ($\text{C}_2\text{H}^3+/\text{C}_3\text{H}^+/ \text{C}_2\text{H}_3\text{O}^+/\text{C}_4\text{H}_3^+/\text{C}_5\text{H}_3+/\text{C}_6\text{H}_2^+/\text{C}_7\text{H}_3^+$, m/z 27/37/43/51/63/74/87) together with K^+
359 (m/z 39) and Na^+ (m/z 23). Carbon fragment ions ($\text{C}^-/\text{C}_2^-/\text{C}_3^- \dots \text{C}_n^-$, m/z -12/-24/-36.....-12_n), CN^-
360 (m/z -26) and sulfate (HSO_4^- , m/z -97) are evident in the negative mass spectra, while nitrate
361 ($\text{NO}_2^-/\text{NO}_3^-$, m/z -46/-62) is dominant in the OC and PAH classes. The presence of internally
362 mixed sulfate is consistent with emissions from the coke plant at the steelworks (Zhang et al.,
363 2021). Mass spectra similar to the three OC-containing classes reported here were also observed

364 downwind of the Port Talbot steelworks (Dall'Osto et al., 2012), with m/z 202 assigned to
365 pyrene/fluoranthene as per previous ATOFMS field studies (Gross et al., 2000b). In the case of
366 Dall'Osto et al. (2012) OC-PAH particles were attributed to the hot and cold mills, while OC and
367 PAH particles were related to the steel/coke-making sector. Thus, all three organic carbon-
368 containing classes are attributed to the steelworks here.

369 **Pb-rich and Li-rich particles:**

370 Average ATOFMS mass spectra for Pb-rich particles are shown in Figure 8, characterized by
371 internally mixed K^+ (m/z 39), Pb^+ (m/z 208), Cl^- (m/z -35) and nitrate (NO_2^-/NO_3^- , m/z -46/-62).
372 No equivalent particles were observed in the ferromanganese facility samples. Pb-containing
373 particles similar to the Pb-rich class were also observed in the Port Talbot study, and represented
374 <1% of the particles ionized. In that case Pb-containing particles were assigned to the hot and
375 cold mills (Dall'Osto et al., 2008). The Port Talbot Pb-containing particles were internally mixed
376 with KCl, which is also the case for Dunkirk as shown in Figure 8. Thus Pb-rich particles are
377 attributed to the steelworks here.

378 Li-Zn particles contain Li^+ (m/z 7), Na^+ (m/z 23), K^+ (m/z 39), Zn^+ (m/z 65/66/68), nitrate (NO_2^-
379 $/NO_3^-$, m/z -46/-62) and phosphate (PO_3^- , m/z -79), as shown in Figure 8, and were not observed
380 in the ferromanganese facility samples. Particles detected by ATOFMS containing Li have been
381 assigned to coal combustion sources in previous studies (Guazzotti et al., 2003; Furutani et al.,
382 2011). Zn-containing particles were also associated with the Port Talbot steelworks, but those
383 particles did not contain internally mixed Li (Dall'Osto et al., 2008). Li-Zn particles have a
384 minimal mass contribution overall and it cannot be easily determined whether they originate
385 from the ferromanganese facility or the steelworks.

386 **3.3 Source Apportionment**

387 Summing the mass concentrations of the different particle classes associated with the
388 ferromanganese facility and the steelworks enabled an estimation of the $PM_{2.5}$ associated with
389 metalworking activities at the receptor site at hourly resolution. Elevated metalworking $PM_{2.5}$
390 concentrations are strongly dependent on northeasterly wind directions, consistent with the
391 locations of the two metalworking facilities (including ore and coal stockpiles), as shown in

392 Figure 9. Elevated non-metalworking (background) $PM_{2.5}$ mass concentrations are observed
393 under northerly, easterly and southerly wind directions, consistent with more diffuse regional
394 background sources. The contribution of metalworking activities to $PM_{2.5}$ at the receptor site
395 ranged from 1-65% over the entire measurement period, with an average contribution of 17%.
396 The average contribution for those periods when wind was predominantly from the northeast
397 (shaded grey periods in Figure 2) is higher, at 28%. The overall average contribution of 17% is
398 somewhat lower than the 28% contribution these two facilities were estimated to contribute to
399 PM_{10} at a site approximately 3 km to the southeast through PMF analysis of filters collected in
400 2003-2005 (Alleman et al., 2010). Although the local metalworking facilities are not the
401 dominant contributor to $PM_{2.5}$ mass at the receptor site, their dominant contributions to toxic
402 metal and PAH-containing particle concentrations is of concern from an exposure perspective
403 (Schroeder et al., 1987; Durant et al., 1996; Majestic et al., 2007; Zhang et al., 2008; Hu et al.,
404 2012). The metalworking facilities were also the dominant contributor to ultrafine particles at the
405 site (Setyan et al., 2019), a size fraction receiving increased attention with respect to its potential
406 toxicological impacts (Ohlwein et al., 2019; Saleh et al., 2019; Sotty et al., 2019).

407 **4 Conclusions**

408 The unique particle mixing states associated with local metalworking facilities identified at the
409 Dunkirk receptor site will be useful for future researchers aiming to apportion particulate matter
410 to metalworking sources in other locations globally. The facilities investigated here use industrial
411 processes that are common in the pyrometallurgic industry (sintering, smelting/reduction in an
412 electric/blast furnace, refining, rolling and crushing of finished product) and therefore can be
413 considered representative of that sector. The number of distinct chemical mixing states identified
414 highlights the complexity and diversity in primary particle composition associated with
415 emissions from metalworking. Particles containing Mn and Ca were associated predominantly
416 with the ferromanganese facility, while particles containing Fe, K, Pb and PAHs were associated
417 predominantly with the steelworks. Internally mixed fluoride was also found to be a useful
418 discriminating marker for identifying ferromanganese firing chimney emissions specifically. The
419 two metalworking facilities combined are estimated to contribute 17% on average to $PM_{2.5}$ mass
420 concentrations at the receptor site during the measurement period, but are the dominant
421 contributors of particles containing transition metals and PAHs; species associated with negative

422 health outcomes. The single particle source apportionment approach used here is also expected to
423 be useful in other regions where the relative contributions of industrial emissions, including
424 metalworking emissions, to ambient PM_{2.5} concentrations need to be assessed. Knowledge of
425 these contributions is particularly valuable for designing effective local air quality strategies.

426

427 **CRedit statement**

428 **Jovanna Arndt**: Investigation, Methodology, Formal Analysis, Visualization, Data curation,
429 Writing- original draft preparation. **Robert M. Healy**: Investigation, Methodology, Formal
430 Analysis, Visualization, Writing- review and editing. **Ari Setyan**: Investigation, Methodology,
431 Writing- review and editing. **Pascal Flament**: Conceptualization, Writing- review and editing,
432 Supervision, Project Administration, Funding Acquisition. **Karine Deboudt**: Investigation,
433 Conceptualization, Writing- review and editing. **Véronique Riffault**: Investigation, Formal
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435 Funding Acquisition. **Laurent Y. Alleman**: Investigation, Writing- review and editing. **Saliou**
436 **Mbengue**: Investigation, Writing- review and editing. **John C. Wenger**: Conceptualization,
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451

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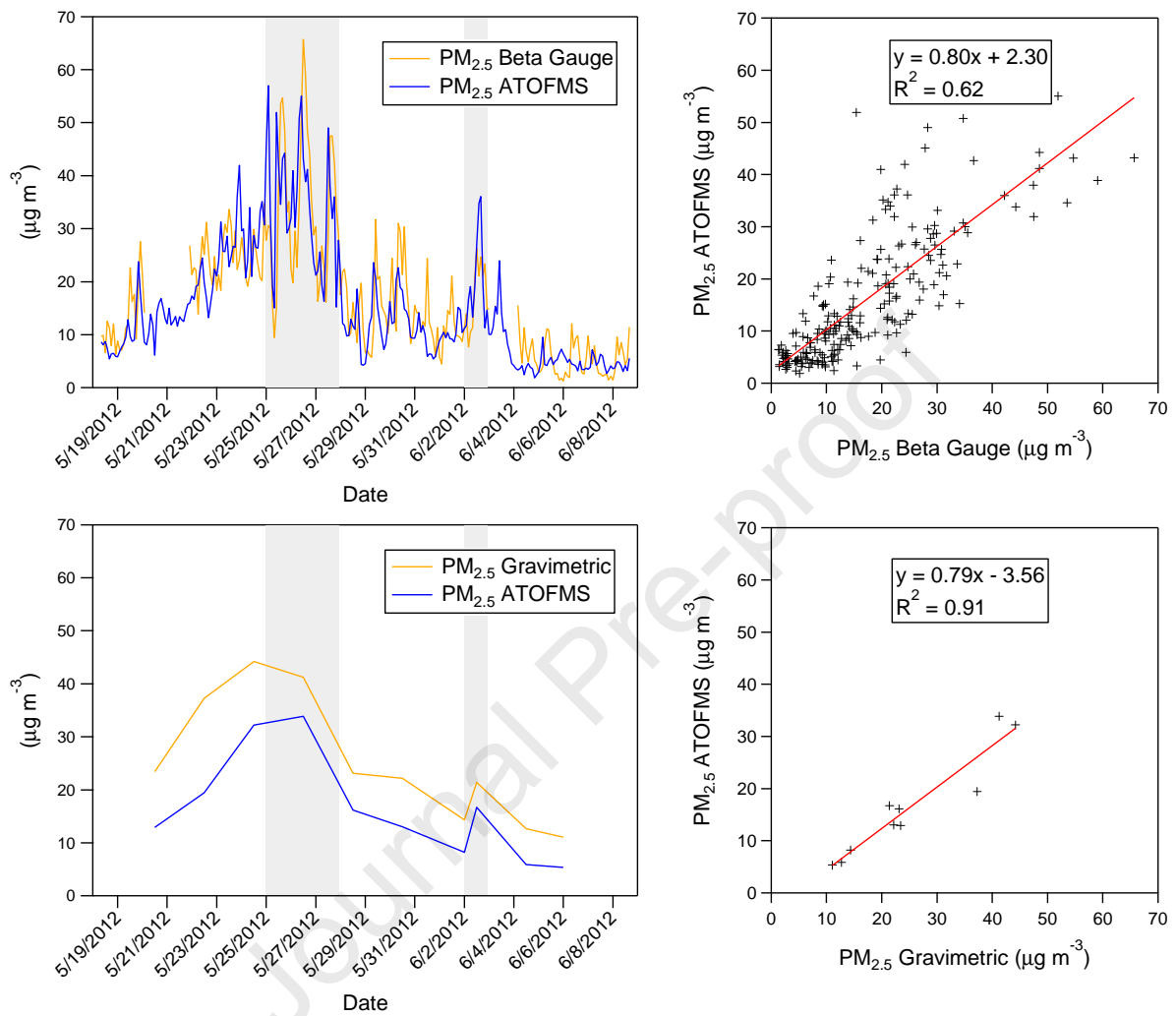
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718 **Figures**

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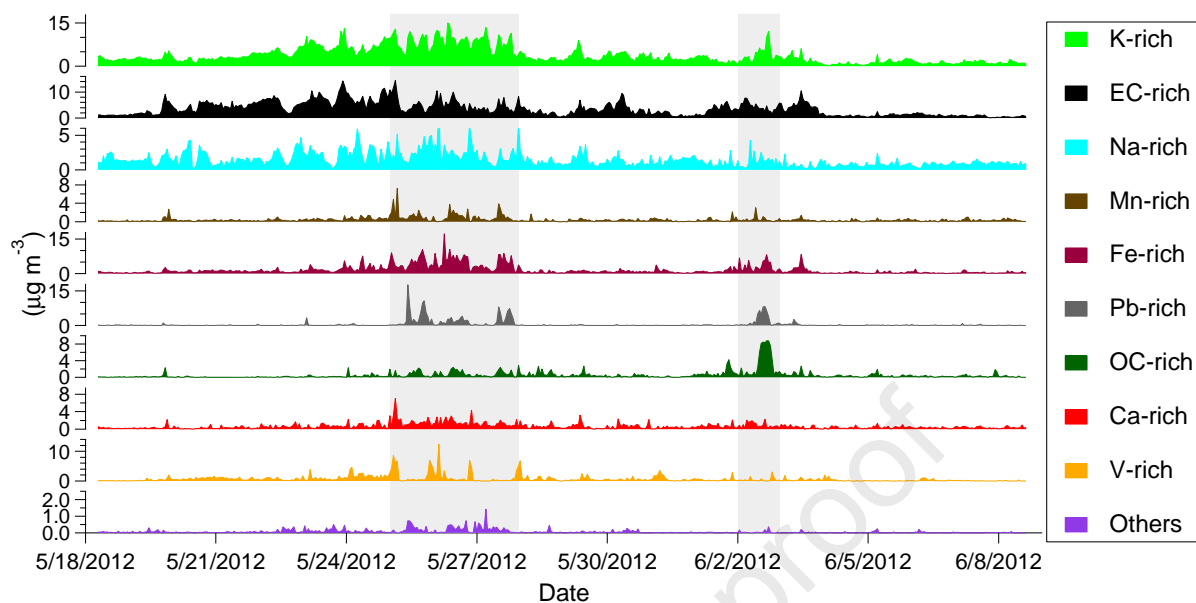
720 Figure 1: Top: Comparison of 2-hour mass concentrations of $PM_{2.5}$ measured by the beta gauge
 721 instrument and derived using the ATOFMS. Bottom: Comparison of 24 to 48-hour mass
 722 concentrations of $PM_{2.5}$ determined by gravimetric filter analysis and derived using the
 723 ATOFMS. Red lines represent least squares regression fits. Days when wind was predominantly
 724 from the northeast (the direction of metalworking facilities) are shaded grey.

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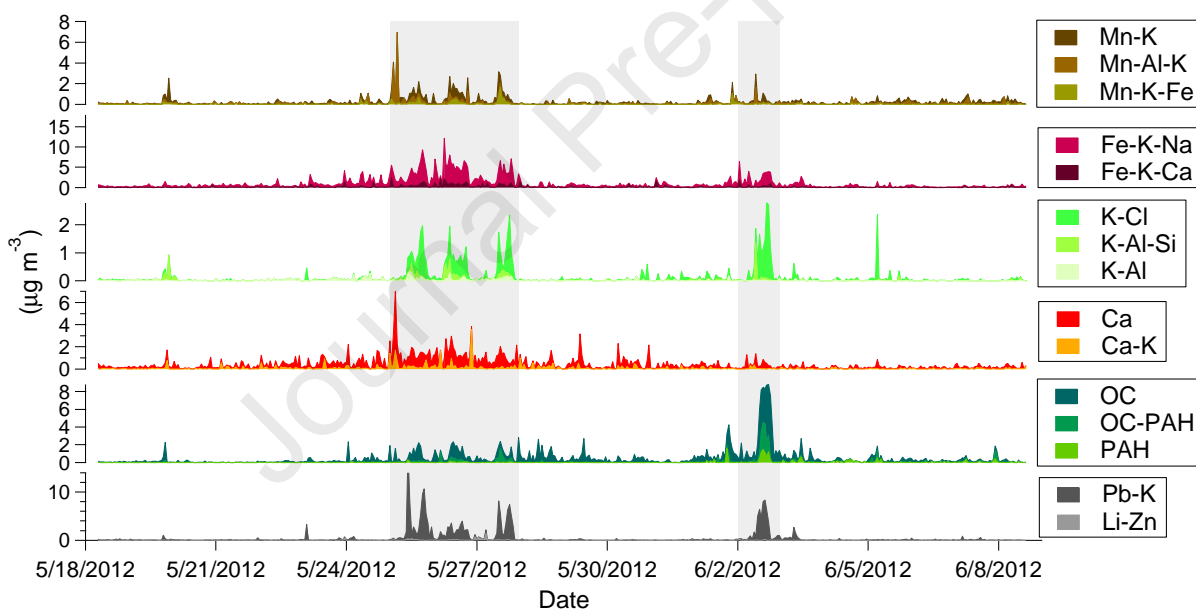
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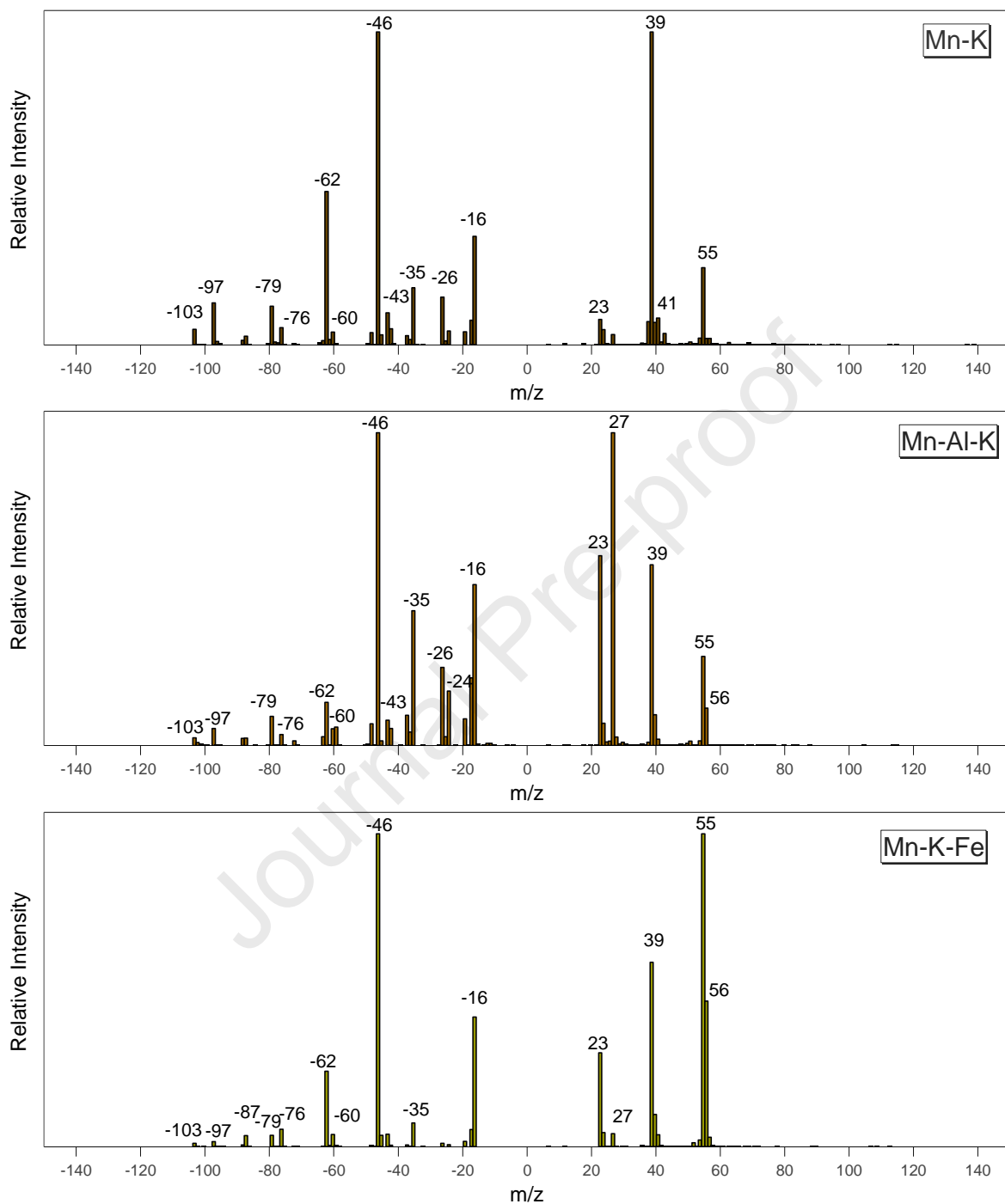


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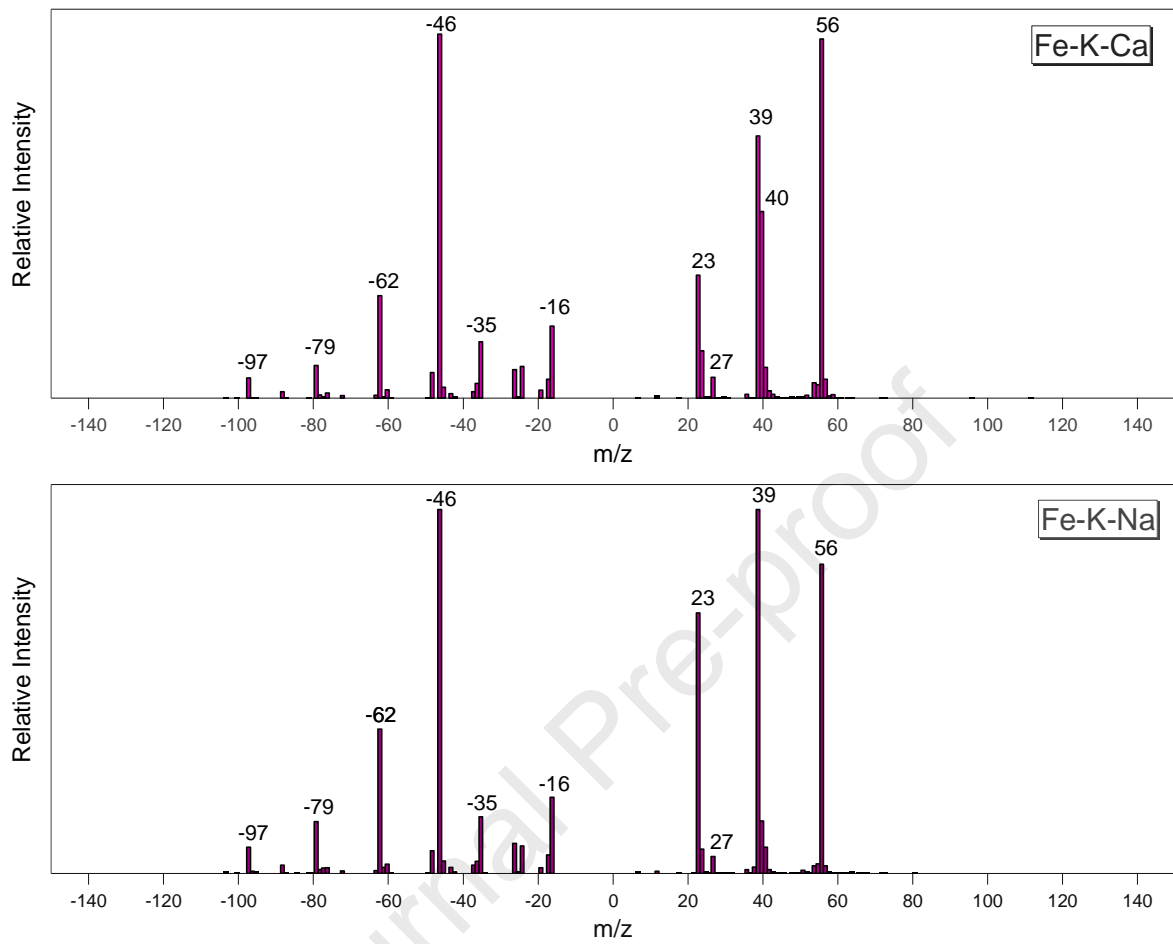
731 Figure 2: Top: Temporal trends of hourly resolution mass concentrations of the ten ATOFMS
 732 particle categories. Bottom: Temporal trends of hourly resolution mass concentrations of
 733 metalworking ATOFMS particle classes. Days when wind was predominantly from the northeast
 734 (the direction of metalworking facilities) are shaded grey.



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736 Figure 3: Average mass spectra for Mn-rich metalworking particle classes.

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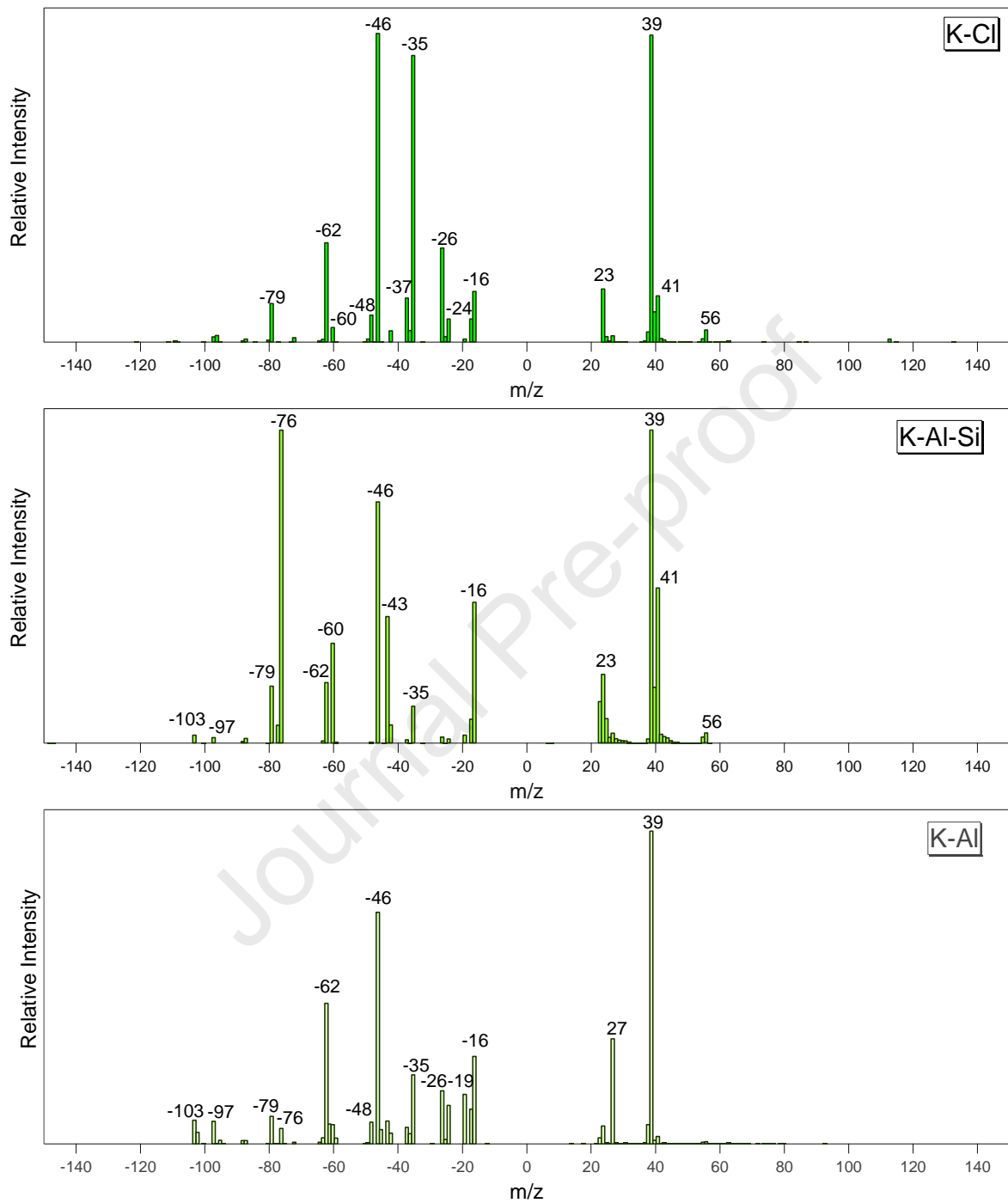
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739 Figure 4: Average mass spectra for iron-rich metalworking particle classes.

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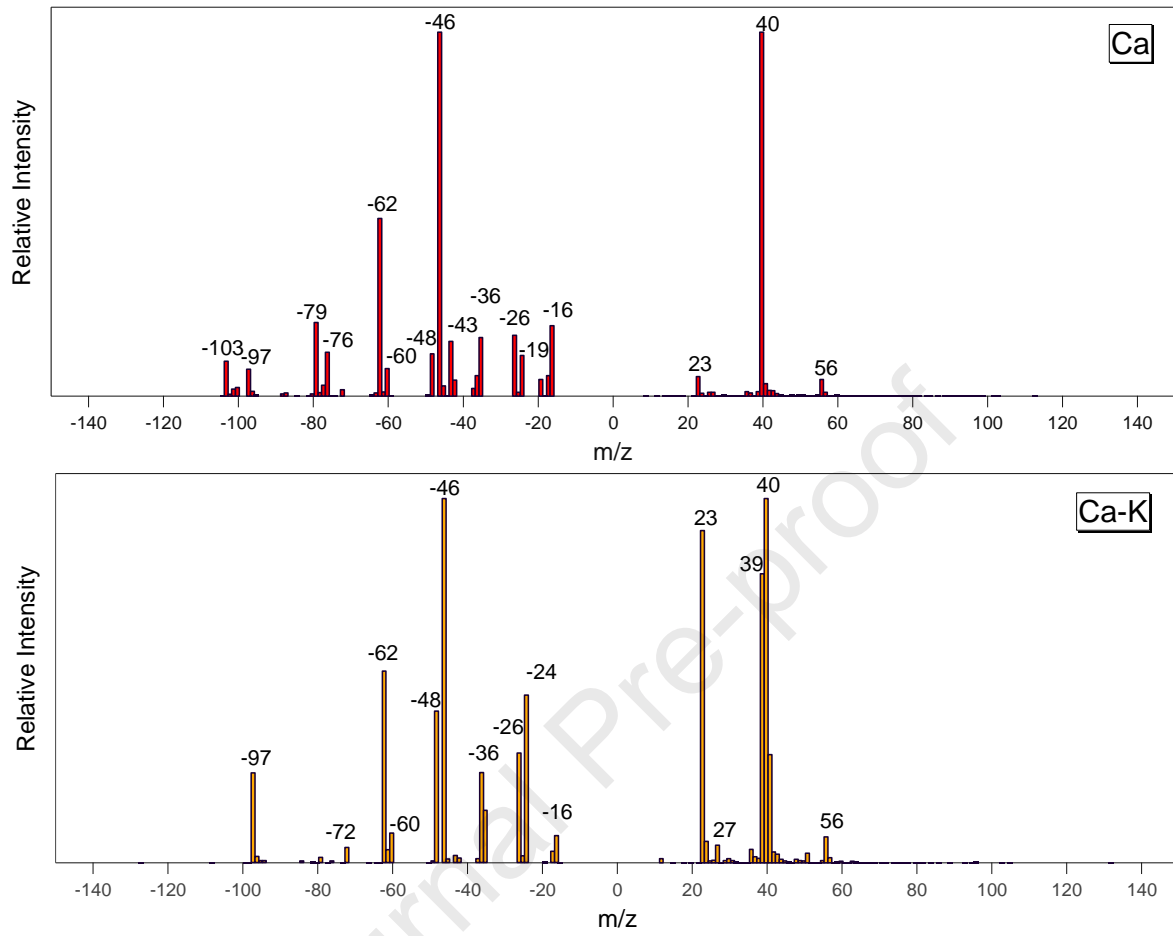
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744 Figure 5: Average mass spectra for K-rich metalworking particle classes.

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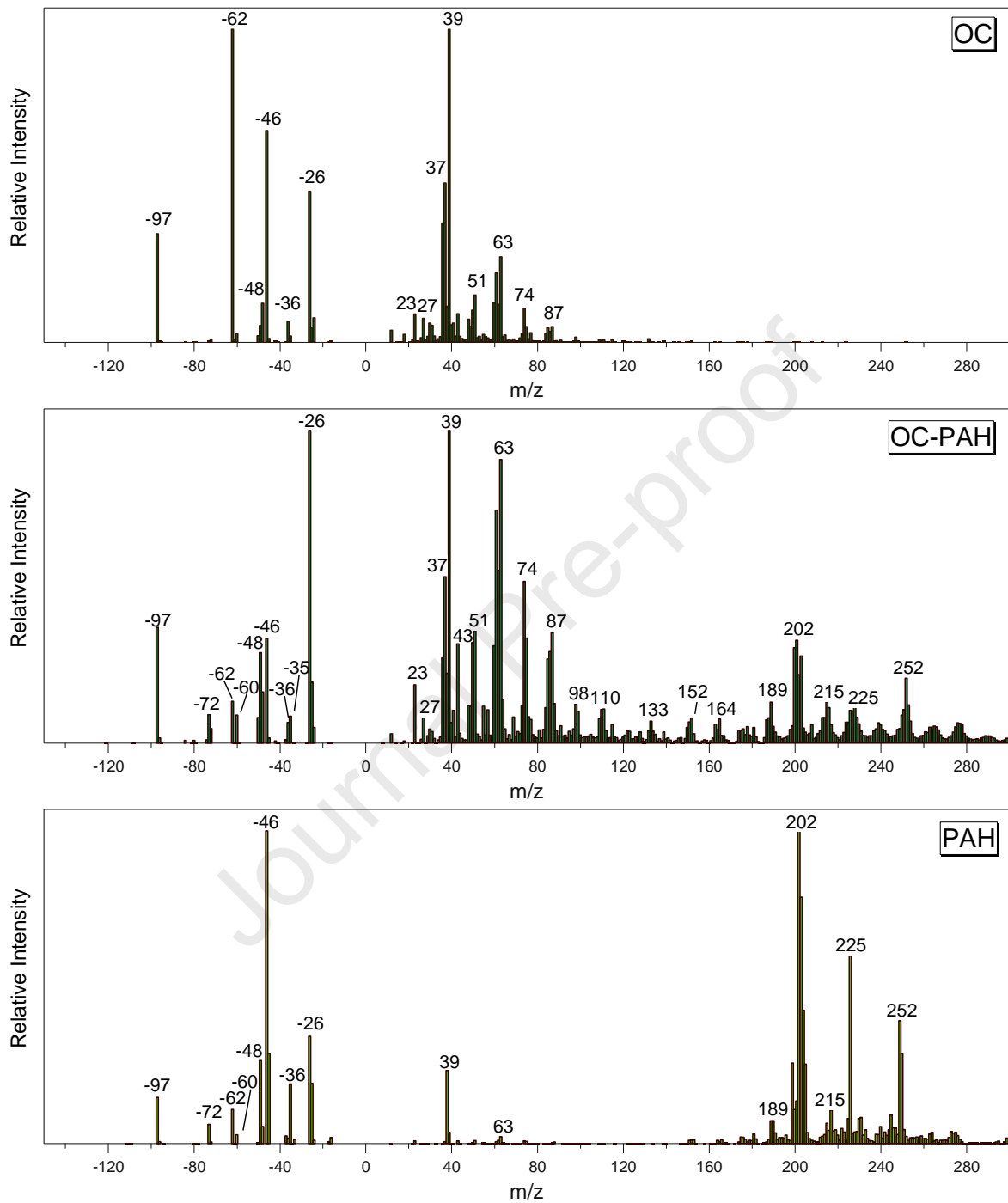
747 Figure 6: Average mass spectra for Ca-rich metalworking particle classes.

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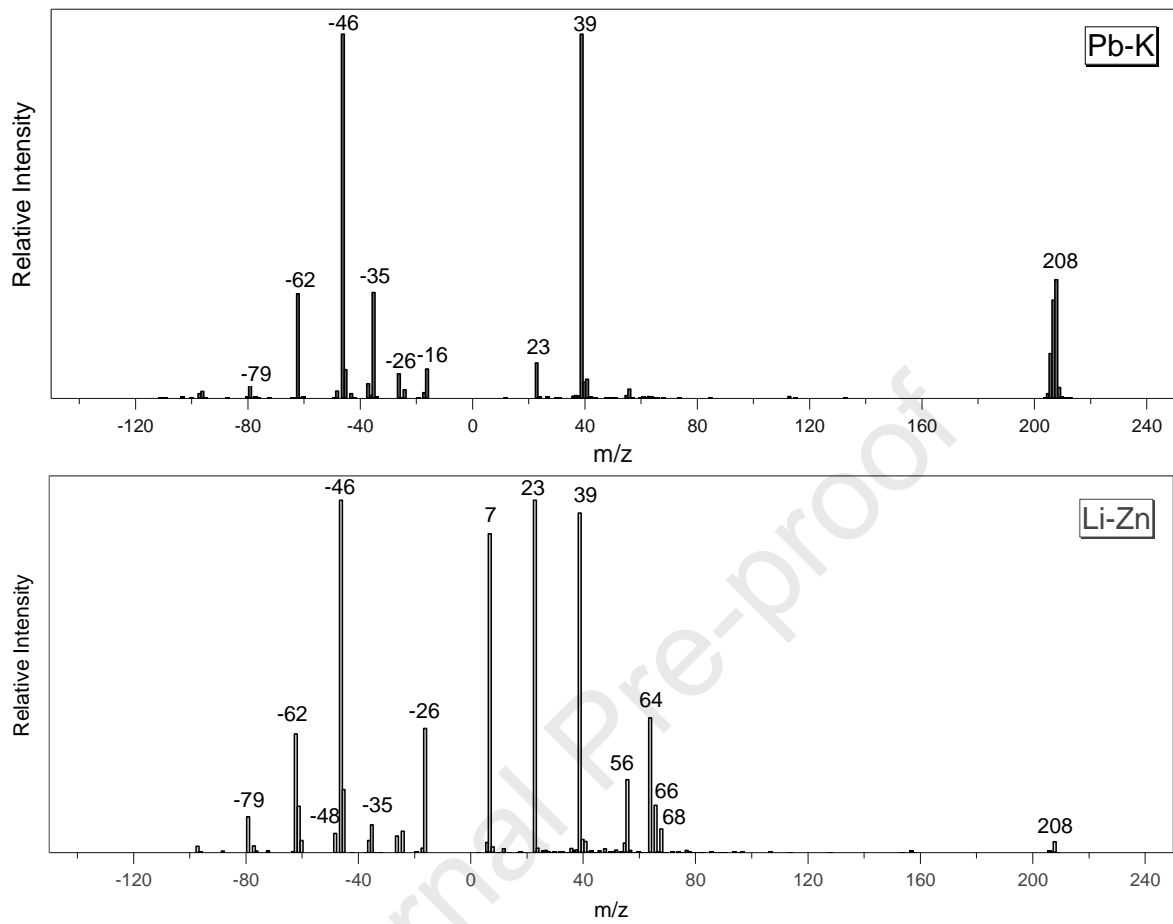
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753 Figure 7: Average mass spectra for OC-rich metalworking particle classes.

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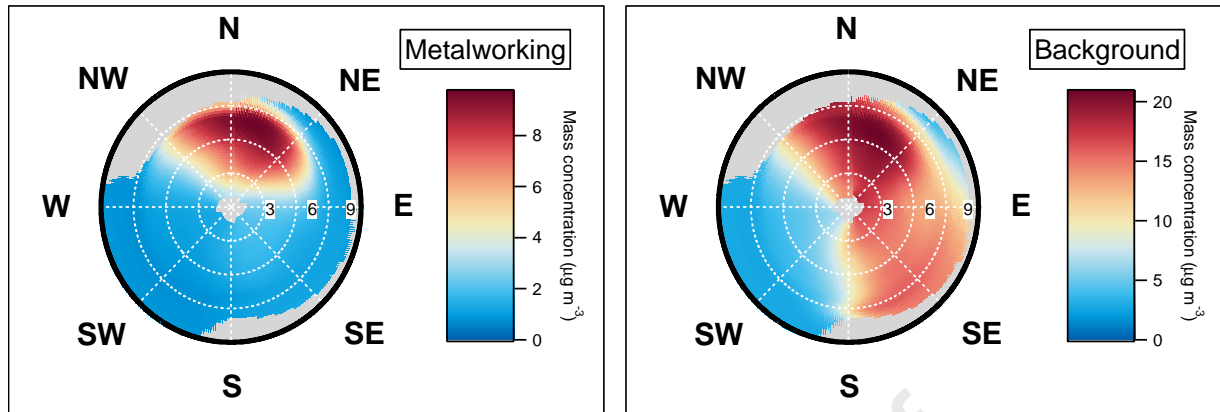
756 Figure 8: Average mass spectra for Pb-rich and Li-rich metalworking particle classes.

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762 Figure 9: Dependence of concentrations of metalworking and background ATOFMS-derived
763 PM_{2.5} mass concentrations upon local wind speed (m s^{-1}) and wind direction. Periods with wind
764 speed $< 1 \text{ m s}^{-1}$ are not included in the analysis. Plots generated using the Zefir Toolkit (Petit et
765 al., 2017) running in Igor Pro v6.37 (Wavemetrics Inc.).

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Highlights

Particles assigned to a ferromanganese facility and a steelworks based on composition

Metalworking particle composition and mixing state is complex and diverse

Metalworking emissions contributed 17% to $PM_{2.5}$ on average at the receptor site

Metalworking is the dominant source of metals and polycyclic aromatic hydrocarbons

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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