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# 1 **Investigation on the near-field evolution of industrial plumes from** 2 **metalworking activities**

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43

44 **Abstract**

45 In a context where a significant fraction of the population lives near industrial areas, the main  
46 objectives of this study are to provide (a) new data on PM<sub>2.5</sub> chemical compositions, heavy-  
47 metal concentrations and trace gases released by metalworking activities and (b) new  
48 information on the near-field evolution (up to about a thousand meters) of such industrial  
49 plumes in terms of particle chemical composition and size distribution. For that purpose, a  
50 one-month field campaign was performed in an industrial area near the city of Dunkirk  
51 (Northern France), combining measurements of atmospheric dynamics and physico-chemical  
52 characterization of air masses. Comparisons between several elemental ratios (mainly Mn/Fe),  
53 particle size distributions and volatile organic compound (VOC) concentrations at the stacks  
54 and at a near-field site suggest that plumes of a ferromanganese alloy plant were quickly  
55 mixed with pollutants emitted by other sources (mainly other industries, possibly traffic and  
56 sea spray), in particular a neighboring steelworks, before reaching the sampling site. This led  
57 to the emergence of secondary particles related to condensation and/or aggregation  
58 phenomena inside the plumes. Metalworking emissions were also identified as a source of  
59 new particle formation, formed through the emission of gaseous precursors and their fast  
60 transformation and condensation, over a timescale of minutes before reaching the near-field  
61 site 800 m downwind. Ultrafine particles emitted at the stacks also quickly agglomerated to  
62 form larger particles before reaching the near-field site. These results show that, even over  
63 short distances, the chemical composition and size distribution of metalworking plumes may  
64 evolve rapidly and the characteristics of particles at the boundary of an industrial area  
65 (especially in contiguous urban areas) may differ from those emitted directly at the stacks.

66

67	<b>Keywords</b>
68	Fine particles
69	Volatile organic compounds
70	Industrial emissions
71	Plume evolution
72	Atmospheric dynamics
73	

## 74 **1 Introduction**

75 Epidemiological studies have demonstrated that exposure to atmospheric pollution has  
76 adverse effects on human health, such as cardiovascular (Brook et al., 2004) and pulmonary  
77 (Oberdörster, 2000) diseases and cancer (Pope et al., 2011). In particular, particles smaller  
78 than  $2.5\ \mu\text{m}$  ( $\text{PM}_{2.5}$ ) are more dangerous than coarse ones ( $\text{PM}_{2.5-10}$ ), because the former can  
79 penetrate deeper into the lungs, reach the alveoli and enter the cardiovascular system (Kelly  
80 and Fussell, 2011). According to the Clean Air for Europe (CAFE, see Table S1 in the  
81 supplementary material for acronyms) program, the average decrease of life expectancy in  
82 Europe due to exposure to  $\text{PM}_{2.5}$  is nine months, but increases to 12-36 months in Benelux  
83 and in the north-east area of France (2005). However, many uncertainties still remain on the  
84 identity of chemicals in the particle phase, their mixing state (which may lead to synergy in  
85 terms of toxicity) and source inventories for fine particles bearing toxic chemicals.

86 Previous studies have shown that industrial activities release large quantities of both gaseous  
87 and particulate matter into the atmosphere. The physico-chemical nature of particles emitted  
88 by industry has already been reviewed (Riffault et al., 2015; Sanderson et al., 2014; Taiwo et  
89 al., 2014). A high variability of chemical composition and size distribution can be observed  
90 depending on the type of industrial processes involved. Nevertheless, tracers of specific  
91 industrial activities, such as heavy metals (Dall'Osto et al., 2008; Wong et al., 2006; Yang et  
92 al., 2018), the organic-to-elemental carbon ratio (OC/EC) (Chow et al., 2011), diagnostic  
93 ratios or concentrations of some specific polycyclic aromatic hydrocarbons (PAHs)  
94 (Katsoyiannis et al., 2011; Leoni et al., 2016), secondary inorganic species such as  
95 ammonium sulfate, nitrate, and chloride (Setyan et al., 2017; Wu et al., 2018), and the carbon  
96 preference index (CPI, defined as the ratio of the sum of odd carbon number of n-alkanes to  
97 the sum of even carbon number of n-alkanes) (Fraser et al., 2002; Li et al., 2010) have been

98 identified as a means by which to provide estimates of the relative contribution of pollutant  
99 sources from heavily industrialized regions. Many industrial activities emit a range of PAHs,  
100 volatile organic compounds (VOCs) and inorganic gases including NO<sub>x</sub> and SO<sub>2</sub>. For  
101 instance, selected industrial processes in steelworks, such as coke production, iron ore  
102 sintering (Ciaparra et al., 2009), and electric arc furnaces (Baraniecka et al., 2010), release  
103 large amounts of PAHs. Coke ovens, commonly used in steelworks, also emit significant  
104 concentrations of VOCs (Lin et al., 2007).

105 In this context, our NANO-INDUS project had two main objectives: 1) to produce new data  
106 on PM<sub>2.5</sub>, carbonaceous particles, heavy-metal concentrations and trace gases released by  
107 metalworking activities; and 2) to provide new information on the chemical composition,  
108 mixing state and source identification of industrial atmospheric particulate matter.

109 In terms of atmospheric processes, NANO-INDUS was motivated by three inter-related  
110 questions:

111 1) How much do the physico-chemical characteristics of atmospheric fine particles at the  
112 boundary of a metalworking industrial complex differ from those directly emitted from the  
113 stacks?

114 2) Is there a link between the presence of fine particles at the boundary of this site and gases  
115 directly emitted from the stacks?

116 3) Do fine particles within a metalworking plume have a homogeneous chemical composition  
117 as essentially primary particles, or are they produced or evolving by condensation and/or  
118 agglomeration, leading to secondary particles with heterogeneous compositions?

119 To help address these questions, a field campaign was conducted at an industrial site close to  
120 the Dunkirk metropolitan area (Grande-Synthe). This region is highly industrialized and the

121 particle concentrations regularly exceed the World Health Organization annual mean  
122 guideline value of  $10 \mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$  (World Health Organization, 2006). Of particular  
123 interest is the industrial area of Grande-Synthe, which is comprised of various industries (steel  
124 industry, metallurgy, smelting works, chemical industry, refineries, food-processing industry,  
125 power production, cement works) (DREAL, 2011) located 7 km from downtown Dunkirk.  
126 Following the diversity of industrial activities at this location, Grande-Synthe is very similar  
127 to many other industrial areas throughout the world, where industrial emissions had also been  
128 studied in previous publications, e.g. at Port Talbot (United Kingdom) (Dall'Osto et al., 2008),  
129 Taranto (Italy) (Amodio et al., 2014), and Hangzhou in the Yangtze River Delta (China) (Dai  
130 et al., 2015). Previous studies have also been performed within the industrial park of Grande-  
131 Synthe (Cazier et al., 2016; Crenn et al., 2017; Mbengue et al., 2015). Particulate metal  
132 content has been extensively studied, due to the importance of steelworks and metallurgy at  
133 Grande-Synthe (Alleman et al., 2010; Arndt et al., 2016; Flament et al., 2008; Hleis et al.,  
134 2013; Kfoury et al., 2016; Landkocz et al., 2017; Marris et al., 2012; Marris et al., 2013;  
135 Mbengue et al., 2014; Mbengue et al., 2017; Santos et al., 2016). A number of elements or  
136 elemental ratios have been used as tracers for specific sources within the industrial area, e.g.  
137 Mn or Mn/Fe ratio for emissions from the ferromanganese alloy factory (Marris et al., 2012),  
138 Pb and Fe isotopes for steelworks emissions (Flament et al., 2008), V and Ni for  
139 petrochemistry (Alleman et al., 2010), Fe, Ca, Al and Mn for selected iron and steel processes  
140 such as sintering, blast furnace, steelmaking and desulfurization slag processing (Hleis et al.,  
141 2013). A few studies have also focused on the measurement of VOCs in this area. For  
142 instance, Badol et al (Badol et al., 2008a; Badol et al., 2008b) identified specific industrial  
143 activities as important sources of benzene (metallurgical, steel industries), octane (lubricant  
144 storage), pentane (hydrocarbon storage), and propene (hydrocarbon cracking). Roukos et al.



145 (2009) measured BTEX (benzene, toluene, ethylbenzene, xylene) during two contrasting  
146 seasons. In winter, BTEX concentrations were mainly due to local pollution, while in  
147 summer, they decreased because of photochemical activity and the influence of continental  
148 aged air masses, highlighting the fact that even in anthropogenically-influenced areas, long-  
149 range transport can have a significant contribution to the observed concentrations. Finally,  
150 Xiang et al. (2012) emphasized the influence of vertical turbulence on the dispersion of VOCs  
151 at the local scale.

152 The aim of the present paper is to give an overview of the measurements performed during  
153 the NANO-INDUS project, and to present the main findings of this study. First, we will  
154 present results obtained during the intensive field campaign performed at the near-field  
155 sampling site, and those obtained during the samplings at the stacks. Then, physico-chemical  
156 characteristics of particles measured when the near-field sampling site was impacted by  
157 plumes from the Fe-Mn plant will be compared to particles measured during periods from  
158 other influences (petrochemistry, urban emissions).

159

## 160 **2 Experimental**

### 161 **2.1 Sampling site**

162 All sampling and measurements took place next to the site of a ferromanganese alloy  
163 manufacturing facility (Fe-Mn plant), located in the industrial area of Grande-Synthe, ~2 km  
164 west of the Dunkirk metropolitan area and ~7 km from the city center (51° 01' 44" north, 2°  
165 16' 10" east, 10 m above sea level). Figure 1a shows a map of the area with the sampling site

166 located centrally within the industrial zone of Grande-Synthe and ~800 m southwest of the  
167 emission chimneys in the Fe-Mn plant.

168 Atmospheric composition at the sampling site can be influenced by a variety of different  
169 emission sources, depending on the wind direction. Pollutant sources to the east of the  
170 sampling site are mainly industrial in origin due to the presence of a large steelworks (< 1  
171 km), but also urban-influenced due to Fort-Mardyck (3'600 inhabitants, ~2 km from the  
172 sampling site) and Dunkirk (93'000 inhabitants, ~7 km from the site). The North Sea is only 1  
173 km to the north and northwest, bringing marine and ship emissions to the site. Approximately  
174 200 m to the north of the site is an outdoor storage area for manganese ores which is a  
175 potential source of dust during windy periods. Finally, pollutant sources to the west  
176 (petrochemistry, glass production) and southwest (refineries) of the site also mainly originate  
177 from industrial activities.

178 The Fe-Mn plant receives iron-enriched manganese ores by boat, and transforms these ores  
179 into a ferromanganese alloy, which is used in steelworks to improve the mechanical properties  
180 of steel. Figure 2 shows a schematic drawing of the production process. In the first step,  
181 manganese ores are sintered with anthracite and calcite ( $\text{CaCO}_3$ ) in an oven. This step  
182 involves heating of the sinter, followed by cooling. In the second step, the manganese ore  
183 included in the sinter is reduced into metallic Mn in an electric arc furnace, which provides  
184 the necessary energy for the redox reaction. The third and last step consists of crushing the  
185 alloy to obtain the final product. Particles and gases emitted during these steps are collected in  
186 three different chimneys, in which they are treated by filters before their release into the  
187 atmosphere. Two of these chimneys are located in the sintering unit, above the firing and the  
188 cooling areas, respectively, while the third chimney is in the smelting unit. The sintering unit  
189 works 24 hours a day with particles and gases continuously emitted from its two chimneys.

190 Emissions from the smelting unit, where electrochemical reduction of the manganese ore and  
191 casting of the final product takes place, occur about once every six hours.

## 192 **2.2 Instrumentation**

193 The field campaign took place between May 15 and June 12, 2012. The complete list of  
194 instruments deployed during this field campaign is given in Table S2. Local meteorological  
195 parameters were measured using a weather station (Davis Instruments, Hayward, CA; model  
196 Vantage Pro 2) and a sonic anemometer (METEK GmbH, Elmshorn, Germany; model USA-  
197 1). A Doppler sonic detection and ranging (SODAR; Remtech, Vélizy, France; model PA2)  
198 instrument was used to determine turbulence and vertical profiles of the wind components. An  
199 aerosol light detection and ranging (LIDAR; Raymetrics S.A., Paiania, Greece) instrument  
200 was installed near the sampling site (Figure 1b). Every 15 minutes, the LIDAR scanned in  
201 four different directions, and the backscattered light was used to determine the particle  
202 abundance as a function of the altitude and the distance from the instrument.

203 A large suite of instruments was set up to characterize the concentration, chemical  
204 composition and size distribution of particles with a high time resolution (~5 minutes). These  
205 instruments were connected to a common isokinetic particle sampler (Alfaro et al., 2003)  
206 operated at  $52 \text{ m}^3 \text{ hr}^{-1}$ , 7 m above ground level. The Particle Loss Calculator (von der Weiden  
207 et al., 2009) was used to calculate particle loss across the sampler (Figure S1 in the  
208 supplementary material). The cut-off size of the sampling line was  $2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ), assuming  
209 an average particle density of  $2.5 \text{ g cm}^{-3}$  based on the measured chemical composition. This  
210 high particle density is due to the fact that the sampling site was impacted by a high fraction  
211 of sea salts, metal oxide particles (Fe, Mn, Al), and  $\text{CaCO}_3$  (see Section 4.1). A high-  
212 resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; Aerodyne Research Inc.,

213 Billerica, MA) (Canagaratna et al., 2007; DeCarlo et al., 2006) measured the chemical  
214 composition and size distribution of non-refractory submicron particles (NR-PM<sub>1</sub>) in the  
215 range 50-1000 nm (in vacuum aerodynamic diameter,  $D_{va}$ ). Since this instrument uses a  
216 thermal method to vaporize aerosol species, refractory materials, such as black carbon, sea  
217 salt and most metallic species, cannot be detected with this technique. An aerosol time-of-  
218 flight mass spectrometer (ATOFMS; TSI Instruments Ltd., High Wycombe, U.K.; model  
219 3800-100) (Arndt et al., 2016; Gard et al., 1997) simultaneously measured single particle  
220 composition and mixing state in the size range 100-3000 nm (in  $D_{va}$ ). The ATOFMS  
221 vaporizes aerosol species by laser ablation, enabling the measurement of refractory species,  
222 which are expected to play a significant role in the particle chemistry at this industrial site.  
223 Over 700'000 single particle mass spectra were collected during the campaign and clustered  
224 using the K-means algorithm (K=90), as described in detail elsewhere (Gross et al., 2010;  
225 Healy et al., 2010; Healy et al., 2009). A 2-wavelength Aethalometer (Magee Scientific,  
226 Berkeley, CA; model AE42) was deployed to measure organic-like (OC) and black carbon  
227 (BC) concentrations via the measurement of absorption coefficients at 370 and 880 nm,  
228 respectively. The algorithm presented by Weingartner et al. (2003) was used to reduce  
229 measurement artifacts due to filter loading and the scattering of the light beam in the filter  
230 matrix. Two scanning mobility particle sizers (SMPS) and an optical particle counter (OPC)  
231 were used to measure the particle size distribution. The first SMPS system (Grimm Aerosol  
232 Technik, Ainring, Germany) was comprised of a differential mobility analyzer (DMA; model  
233 55-900) and a condensation particle counter (CPC; model 5.403), enabling particle counting  
234 in the size range 10-1000 nm (in mobility diameter,  $D_m$ ), while the second SMPS (TSI Inc.,  
235 Shoreview, MN) was constituted of a CPC model 3010, an electrostatic classifier model 3080,  
236 and a DMA model 3081, enabling particle counting in the size range 10-480 nm (in  $D_m$ ). The

237 OPC (Grimm Aerosol Technik; model 1.108) measured particles in the size range 300 nm -  
238 20  $\mu\text{m}$  (in optical diameter).

239 In addition to the above-mentioned instruments for online particle measurements, several  
240 cascade impactors (Dekati Ltd., Tampere, Finland; 13-stage low pressure impactor, and 3-  
241 stage  $\text{PM}_{10}$  impactors) and a speciation sampler (Thermo Fisher Scientific, Waltham, MA;  
242 model Partisol 2300) were also deployed to sample particles on filters for subsequent off-line  
243 analyses. These results, some of which have already been published (Mbengue et al., 2014),  
244 included the measurement of metals by inductively-coupled plasma mass spectrometry  
245 (ICP/MS) (Varian Inc., Santa Clara, CA; model 820-MS; or Perkin Elmer, Waltham, MA;  
246 model DRC Elan 6100) and by inductively-coupled plasma atomic emission spectroscopy  
247 (ICP/AES) (IRIS Intrepid, Thermo-Scientific), and organic carbon (OC) and elemental carbon  
248 (EC) by a thermal-optical method (Sunset Laboratory, Tigard, OR; Lab OC-EC aerosol  
249 analyzer).

250 A proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Kore  
251 Technology Ltd, Ely, Cambridgeshire, U.K.; model Series I) (de Gouw and Warneke, 2007;  
252 Lindinger et al., 1998) allowed for measurement of VOCs with a proton affinity higher than  
253 that of water. Long-chain alkanes and aldehydes ( $>\text{C}_8$ ) were sampled on adsorbing cartridges  
254 with an automatic sampler, and analyzed after thermal desorption by gas chromatography  
255 coupled to a mass spectrometer (GC/MS) (Agilent Technologies Inc., Santa Clara, CA; GC:  
256 model 6890N; MS: model 5975) following a procedure previously developed and validated  
257 (Detournay et al., 2011). Finally, automatic analyzers were used to monitor  $\text{CO}_2$  (Horiba Ltd,  
258 Kyoto, Japan; model VA-3000) as well as CO (model CO 12M),  $\text{NO}_x$  (model AC 31M),  $\text{O}_3$   
259 (model  $\text{O}_3$  41M), and  $\text{SO}_2$  (model AF 22M), all from Environnement S.A., Poissy, France.

260 Sampling at the stacks of the ferromanganese alloy production facility was performed using  
261 automatic analyzers for gases (SO<sub>2</sub>, CO, NO<sub>x</sub>), cascade impactors and adsorbing cartridges  
262 for collection of particles and VOCs/PAHs for subsequent off-line analysis (Table S3). PM  
263 was collected in the flues of each stack (downstream of the industrial filters) by installing a 3-  
264 stage cascade impactor (Dekati Ltd) into the center of the chimney flue. The impactor was  
265 equipped with a vertical PM<sub>10</sub> sampling head and the sampling rate was adapted to the stack  
266 flue in order to obtain an isokinetic sample. This sampling meets European standards for stack  
267 dust sampling for emission controls. More details can be found elsewhere (Arndt et al., 2016;  
268 Mbengue et al., 2014).

269 Date and time are reported in Coordinated Universal Time (UTC). The local time during this  
270 study was Central European Summer Time (CEST), which corresponds to UTC+2:00.

271

## 272 **3 Meteorology**

### 273 **3.1 Meteorological conditions and atmospheric dynamics**

274 Figure 3 shows the time series of standard meteorological parameters (temperature, relative  
275 humidity, solar radiation, rainfall, wind direction and speed) observed during the  
276 measurement period, along with atmospheric stability, while back trajectory analysis is  
277 presented and discussed in the supplementary material (Figures S2-S4). The temperature  
278 varied between 6 and 24°C, but for most of the field campaign, was in the range 10-15°C. The  
279 maximum solar radiations were in the range 750-850 W m<sup>-2</sup>. Several occasional rainy periods  
280 occurred during the field campaign, especially after June 2. The relative humidity was rather  
281 high (mean ± 1 σ: 78.9 ± 14.3%) due to the coastal location of the receptor site.

282 The wind direction was an important parameter to identify periods during which the site was  
283 under the influence of metalworking emissions, and in particular when NE winds could  
284 transport plumes from the emission stacks of the Fe-Mn plant to the sampling site. The wind  
285 direction was variable during the field campaign, as shown by the wind rose plot (Figure 1c).  
286 Three dominant wind directions each with an occurrence rate of 15-20% were observed,  
287 corresponding to winds blowing from the southwest, northwest, and north. The wind was  
288 northeasterly for about 5% of the field campaign, and we identified two periods during which  
289 the plume could be transported to the site from this direction: May 25-27, and June 2. The  
290 period between May 25 and 27 was the longest period with a NE wind, corresponding to the  
291 hottest days of the campaign and elevated solar irradiation ( $\sim 800 \text{ W m}^{-2}$ ), which could  
292 increase photo-oxidation and promote relatively faster chemical transformations of particles  
293 and precursor gases between the emission stacks and the sampling site. Moreover, a high  
294 temperature gradient also promotes sea breezes, and thus a vertical mixing of the plumes (see  
295 below).

296 During these NE wind periods, it is important to assess the stability of the atmosphere, which  
297 describes the mixing of emissions over a large area and explain the vertical and horizontal  
298 dispersion of the plume. In the current study, the Monin-Obukhov length scale (deduced from  
299 the sonic anemometer), which depends mainly on heat and momentum fluxes, friction  
300 velocity and temperature, has been used to estimate the atmospheric stability classes (Stull,  
301 1988). Figure 3d shows the time series of the atmospheric stability during the whole  
302 campaign. High occurrences of unstable periods were observed and represent  $\sim 47\%$  and  $17\%$   
303 of unstable and very unstable atmospheric conditions, respectively, thus favoring plume  
304 dispersion. Moreover, LIDAR measurements can confirm this dispersion effect, and that  
305 plumes effectively reach the sampling site during NE wind periods (see below).

306 Winds were blowing from NW to NE on 18 days during the campaign, while 11 sea breeze  
307 events were also observed. Sea breezes have been frequently observed at Dunkirk during  
308 previous studies (Boyouk et al., 2011; Roukos et al., 2011; Talbot et al., 2007). Sea breeze  
309 coming from the sea toward the land may modify the lower troposphere stratification by the  
310 formation of a thermal internal boundary layer (TIBL) (Augustin et al., 2006). The TIBL is a  
311 thin unstable layer where pollutants can be trapped and mixed. Furthermore, since the  
312 SODAR echo depends on fluctuation of temperature due to the signature of the boundary  
313 layer top, the TIBL top, characterized by high echo values, can be detected (Beyrich, 1997).  
314 During the present campaign, the NE wind period between May 25 and May 27 is of  
315 particular interest, because according to the wind direction and wind speed time-height  
316 sections from the SODAR (Figure 4a), these three days are characterized by long sea breeze  
317 events (e.g. on May 25 from 10:00 am to 8:00 pm, on May 26 from 9:00 am to 8:00 pm, and  
318 on May 27 from 11:00 am to 8:00 pm), with winds at ground level coming mainly from the  
319 NE and likely transporting plumes from the Fe-Mn plant to the sampling site. According to  
320 Figure 4e, these sea breeze events are also characterized by an increase in the concentration of  
321 particulate phase organics and ammonium nitrate, and a decrease in the concentration of  
322 sulfate. These results suggest that organics and ammonium nitrate could possibly be emitted  
323 by metalworking activities.

### 324 **3.2 Detection and monitoring of metalworking plumes**

325 Ground-based remote sensing instruments (SODAR and LIDAR) were used to monitor the  
326 propagation of metalworking plumes in the vicinity of the sampling site. Figure 4 includes the  
327 SODAR, LIDAR, AMS, Aethalometer, and SMPS data during the period 25-27 May when  
328 the winds were from the NE and sea breezes were observed, while Figure S5 shows a few



329 examples of LIDAR vertical scans for four relevant directions. The LIDAR data shown in  
330 Figures 4b and S5 correspond to the depolarization ratio at 355 nm, i.e. the ratio between the  
331 measured perpendicular and parallel backscattered LIDAR signals. This parameter provides  
332 information in order to distinguish spherical (e.g. haze) from non-spherical particles (e.g. dust  
333 and smoke) in the atmosphere. For example, non-spherical particles as industrial dust (e.g. fly  
334 ash from metalworking or steelworks) can depolarize LIDAR signals, resulting in high  
335 depolarization ratio values. The higher 355 nm-depolarization ratios were observed during 25-  
336 27 May sea breeze events (Figure 4b), clearly indicating that during these precise time slots  
337 our sampling site was influenced by metalworking plumes.

338 To confirm the identification of periods during which the sampling site was specifically  
339 impacted by these plumes, a two-steps analysis of SODAR and LIDAR data was performed.  
340 First, the SODAR data (Figure 4a) was used to determine periods during which the wind at  
341 ground level was coming from the NE. Then, the LIDAR data for these periods (Figures 4b  
342 and S5) was used to determine whether the sampling site was under the influence of the  
343 plumes, as well as to confirm the origin of these plumes. For instance, Figure S5d shows a  
344 LIDAR vertical scan measured toward an azimuth angle of  $228^\circ$ , corresponding to the  
345 direction of the sampling site (Figure S5e). This scan shows that a plume was located very  
346 close to the sampling site. LIDAR scans measured less than an hour earlier toward the stacks  
347 (azimuth angle  $13^\circ$ , Figure S5a) and the azimuth angles  $308^\circ$  (Figure S5b) and  $238^\circ$  (Figure  
348 S5c) helped us to determine that the plume was mainly coming from the stacks of the Fe-Mn  
349 plant, possibly mixed with emissions from the nearby steelworks.

350

## 351 4 Results and discussion

### 352 4.1 Particle chemical composition

353 Figure 5b shows the time series of the five NR-PM<sub>1</sub> species measured by the HR-ToF-AMS,  
354 along with BC measurements from the Aethalometer. The average NR-PM<sub>1</sub> concentration  
355 during the study was 10.7  $\mu\text{g m}^{-3}$ . This mean value, taking only NR-PM<sub>1</sub> into account, slightly  
356 exceeds the WHO recommendations (10  $\mu\text{g m}^{-3}$ ). Concentrations were very high between  
357 May 24 and May 27 (in the range 20-75  $\mu\text{g m}^{-3}$ ), but decreased significantly after June 5  
358 (below 5  $\mu\text{g m}^{-3}$ ). According to meteorological conditions and atmospheric dynamics during  
359 these periods (Section 3), high mass loadings were concurrent with low wind speed coming  
360 from the northeast and east (metalworking activities sector), while the decrease in particle  
361 mass loading during the last week occurred when the wind speed increased significantly and  
362 wind direction shifted to the south, bringing a few rain episodes. NR-PM<sub>1</sub> was dominated by  
363 inorganic species, which accounted for  $\sim 2/3$  of the total mass, while organics accounted for  
364  $\sim 1/3$  (Figure 5, upper pie chart). However, the chemical composition varied significantly  
365 throughout the study, and several pollution events dominated by ammonium nitrate,  
366 ammonium sulfate or organics were observed, especially downwind of metalworking  
367 emissions. Despite the fact that very few studies emphasized the contribution of non-  
368 refractory submicron aerosols (NR-PM<sub>1</sub>) to metalworking (steel industry, metallurgy,  
369 smelting works) emissions (Almeida et al., 2015; Crenn et al., 2017), this confirms the  
370 importance of secondary aerosols in these emissions. We also observed several periods with  
371 an increase in the non-refractory chloride concentration up to  $\sim 5 \mu\text{g m}^{-3}$ . This chloride does  
372 not correspond to sea salt, given that the AMS, operated in standard conditions (with the  
373 vaporizer set at 600°C), cannot evaporate and measure NaCl. Examination of the dependence

374 of chloride mass concentrations upon wind direction indicates that this species was observed  
375 only during NE wind periods, i.e. when the sampling site was under the direct influence of the  
376 Fe-Mn plant and the adjacent steelworks. Moreover, chloride was found to be very well  
377 correlated with the  $K^+$  fragment of the AMS ( $r^2=0.67$ ), suggesting that chloride was mainly  
378 present in the form of KCl. This might be due to the high formation of KCl during the  
379 sintering process in steelworks (Hleis et al., 2013; Ji et al., 2017; Peng et al., 2009) and is  
380 consistent with previous observations using the same instrument at a nearby location (Crenn  
381 et al., 2017). Thus, the non-refractory chloride signal may be a useful proxy to determine  
382 periods during which a receptor site is under the influence of emissions from steelworks.

383 This is confirmed by complementary data obtained using the ATOFMS (Figure 5c), which  
384 identified 34 distinct particle classes that were subsequently grouped into 10 general  
385 categories for clarity. Sea salt particles dominated the dataset by number (24.4% of total  
386 spectra), followed by K-containing particles (23.2%) and EC (23.1%). The remaining particle  
387 classes correspond to Fe-containing (5.0%), Ca-containing (1.7%), OC and PAH-containing  
388 (1.7%), V-containing (1.4%), Mn-containing (1.2%), Pb-containing (1.1%), and other metals  
389 (17.1%, including Zn and, in addition, S- and amine-containing particles). Most particle  
390 classes are associated with industrial sources (Arndt et al., 2016), based on their composition  
391 and wind dependence. K-containing particles are usually associated with biomass burning  
392 sources, especially in winter in this region, however domestic wood burning is expected to be  
393 negligible at this time of year (May/June). The significant abundance of K-containing  
394 particles is consistent with the high signal for non-refractory chloride observed by the AMS  
395 and confirms the importance of steelworks sintering emissions containing KCl. EC particle  
396 numbers increased towards the end of the sampling period, while OC and PAH-containing  
397 particles were detected in their largest numbers on June 2. EC-containing particles were more

398 plentiful during E-NE wind periods (Figure 5a-c), i.e. when the sampling site was more  
399 specifically under the influence of the nearby coke production facility of the integrated  
400 steelmaking plant. Weitkamp et al. (2005) showed that elemental carbon contributes up to 30  
401 wt.% to coke production emissions. Ca-containing, Fe-containing and Mn-containing particles  
402 clearly increase on May 25, 26 and 27 (downwind of the metalworking emissions), while the  
403 latter two categories (Fe- and Mn-containing particles) also increased sharply on May 17,  
404 under the influence of urban emissions. Given their composition and size, particles in these  
405 categories are almost certainly emitted by either the ferromanganese alloy production plant or  
406 the neighboring steelworks. This is supported by the fact that these particles are detected in  
407 higher numbers during periods when meteorological conditions were most favorable for  
408 plumes to be transported from these two plants, as monitored by LIDAR sensing (see Section  
409 3.2). Further discussion and interpretation of the ATOFMS data, including the other metals  
410 category, will be the subject of future publications.

411 Figure 6 represents the time series of size-resolved elemental composition, determined by  
412 ICP/MS and ICP/AES analysis of filters collected using a 13-stage impactor with a time  
413 resolution of 24 or 48 hours, while Figure 7a shows the time series of the mass concentration.  
414 The concentration of the following elements increased significantly during the periods May  
415 25-27 and June 1-3, when the wind was predominantly coming from the metallurgical  
416 complex (NE winds): Fe, Mn, Ca, K, Zn, Pb, plus a few minor elements (Cu, Ti, Ba, Rb, Sr).  
417 The size distribution indicates that some elements are enriched in the submicron fractions, (K,  
418 Zn, Pb, V, Ni, Cr, Rb, Mo, As, Cd, Sb), while others are more abundant in the coarse fraction  
419 (Fe, Ca, Mn, Ti, Ba, Sr), depending on the wind direction. The fact that both Mn and Fe,  
420 abundant downwind of ferromanganese- and steelworks-emissions, were more concentrated  
421 in the coarse fraction may be due to a combination of (i) the resuspension of dust from the

422 iron-enriched manganese ores stored outdoors (Figure 1b), (ii) industrial mechanical  
423 processes (excavating, crushing or ore pile processing), in addition to stationary emissions  
424 (sintering, etc.), and (iii) road dust resuspension in the harbor area. The comparison between  
425 elemental ratios at the emission stacks of the Fe-Mn alloy plant and at the sampling site has  
426 been used to confirm periods during which the sampling site was under the influence of  
427 emissions from this plant (Table 1). Among the three plant stacks, the one located above the  
428 cooling area of the sintering unit (stack B, Figure 2) was by far the most important emitter of  
429 fine particles (Arndt et al., 2016), ~4 times more than stack A (firing area) and ~50 times  
430 more than stack C (smelting unit) (Figure 7b). Given that the plant was manufacturing  
431 ferromanganese alloy, the most suitable proxy for our analysis is the Mn/Fe ratio (Marris et  
432 al., 2012). Emissions from the stacks of the plant show an enrichment of Mn compared to Fe,  
433 with a Mn/Fe ratio around 3 (Table 1). At the near-field site, the Mn/Fe ratio remained below  
434 1, except for two periods (May 19-21 and May 31-June 1) when both metal concentrations  
435 were very low. In addition, the Mn/Fe ratio during the two periods under the influence of NE  
436 winds (May 25-27 and June 1-3) was in the range 0.3-0.4. This result, coupled with the  
437 increase of potassium from KCl (steelworks sintering emissions proxy) observed by the HR-  
438 ToF-AMS during the same periods, suggests that the plumes emitted by the Fe-Mn plant were  
439 mixed, before reaching the sampling site, with emissions from the adjacent steelworks, for  
440 which the Mn/Fe ratio is very low ( $<0.01$ ) (Alleman et al., 2010). Other elemental ratios  
441 reported in Table 1 show that values calculated for the near-field site are very different from  
442 those determined at the stacks, suggesting that the plumes were quickly (within a few  
443 minutes) mixed with pollutants emitted by other sources (e.g. steelworks, truck traffic in the  
444 industrial zone) (Mbengue et al., 2017) before reaching the sampling site. This is certainly  
445 due to the unstable atmospheric conditions prevailed most of the time during the sampling

446 campaign (Figure 3d), favoring plumes dispersion. This is especially true during sea breeze  
447 events, with the formation of an unstable TIBL, as those unambiguously identified during the  
448 May 25-27 period, the longer sea breeze episode of the field campaign.

#### 449 **4.2 Particle size distributions**

450 Figure 8 shows the time series of the particle number size distribution between 10 and 500  
451 nm, along with the average size distribution for the entire study. The average size distribution  
452 has a single mode at 40 nm (in  $D_m$ ). However, the particle number concentrations and size  
453 distributions varied dynamically during the study. Several periods displayed an increase in the  
454 particle number concentration. During most of these periods, size distributions were unimodal  
455 with a mode centered at 40-60 nm (e.g. May 19, 28, 29, 30, June 1). However, size  
456 distributions observed during NE wind periods (May 25-27, June 2) were very different, and  
457 showed a mode at much smaller sizes, below 20 nm. This observation was also quite obvious  
458 during sea breeze events on May 25-27 (Figure 4d), systematically associated with an  
459 increase in particles of small sizes centered at around 20 nm. The presence of this nucleation  
460 mode when the sampling site was under the direct influence of metalworking emissions  
461 suggests the occurrence of new particle formation events. New particle formation is a  
462 phenomenon which has been extensively observed at various urban, remote, and coastal  
463 locations (Curtius, 2006; Holmes, 2007; Kulmala et al., 2004; Zhang et al., 2012). Thus, these  
464 events may occur in polluted as well as in very clean environments. Usually, when new  
465 particle formation and growth events occur at a regional scale, the SMPS data trend line  
466 shows a “banana shape”. Indeed, an increase of the concentration of very small particles (<15  
467 nm) is first observed when these new particles are formed. Then, an increase of the mode is  
468 observed during the following hours, when gaseous compounds with low volatility condense

469 onto the surface of these new particles, or when these particles agglomerate to form bigger  
470 ones (Setyan et al., 2014; Setyan et al., 2012). The absence of “banana shapes” and the  
471 presence of a constant nucleation mode during several hours in the present SMPS dataset  
472 (Figure 4d) suggest that new particle formation was due to continuous emissions from a single  
473 point source, located at a constant distance from the near-field sampling site. This may be due  
474 to major emissions of these new particles or gaseous precursors from the Fe-Mn plant stacks  
475 (or adjacent steelworks emissions), which undergo rapid cooling in the ambient air, thus  
476 promoting fast condensation of the gaseous emissions and transformation of stack pipe  
477 generated particles, before reaching the sampling site.

478 Another evidence for new particles formation and growth is emphasized by mass size  
479 distribution measurements. Figure 7a shows the mass size distributions determined at the  
480 sampling site with the 13-stage impactor.  $PM_{2.5}$  concentrations varied in the range of 11-44  
481  $\mu\text{g m}^{-3}$  during this study. The highest concentrations observed during the whole field  
482 campaign were reached when the wind was coming from the NE direction at relatively low  
483 speed, which counteracted dilution of the plumes. The total mass was dominated by  
484 submicron particles (from 0.1 to 1  $\mu\text{m}$ ), which accounted for 63.1% of the mass, while  
485 particles larger than 1  $\mu\text{m}$  accounted for 33.5%. Particles in the ultrafine size range ( $<0.1 \mu\text{m}$ )  
486 had a negligible contribution to the mass (3.4%), even if their number was much higher than  
487 particles of larger sizes. The mass size distributions did not fluctuate drastically during the  
488 study, except for two periods. Between May 15-17, the mass was dominated by coarse  
489 particles (65% of the total, with probably a high contribution of sea salts, considering the  
490 wind direction and results from ATOFMS and ICP/MS – Figures 5c and 6), while from May  
491 29-31, the contribution of submicron particles was higher (77% of the total mass).

492 These size distributions observed at the near-field site were very different to those observed at  
493 the stacks of the Fe-Mn plant (Figure 7b). Emissions from the plant were totally dominated by  
494 particles in the ultrafine range (60.1% of particles  $<0.1 \mu\text{m}$ ), while these particles accounted  
495 for only 3.4% at the near-field site. These observations provide further evidence to support the  
496 fast evolution of the plumes and also indicate that emissions from the stacks are likely very  
497 quickly diluted in an air mass containing larger particles before reaching the sampling site. In  
498 the presence of those larger particles, ultrafine particles freshly emitted at the stacks may  
499 quickly agglomerate to form larger particles before reaching the sampling site. In summary,  
500 ultrafine particles ( $D_m \sim 20 \text{ nm}$ ) seem to be continuously generated by Fe-Mn plant and  
501 steelworks emissions, but within the plumes fast agglomeration processes could result, in a  
502 few minutes, in the formation of larger particles in the accumulation mode ( $0.1\text{-}1.0 \mu\text{m}$ ).

### 503 **4.3 Trace gases**

504 Figure 5f-h shows the time series of several VOC families (aromatics, alkanes, alkenes,  
505 oxygenated VOCs, biogenic VOCs). Most of them exhibited high concentrations during the  
506 first five days of the campaign (May 15-19), then decreased significantly until the end of the  
507 study. However, some short events are also apparent, especially during the NE wind periods,  
508 i.e. under the influence of metalworking activities. Benzene was the only VOC to increase  
509 significantly when the sampling site was under the influence of emissions from the Fe-Mn  
510 plant and steelworks. Toluene also increased during these periods, but to a lesser extent.  
511 Toluene and benzene were by far the most concentrated VOCs released from the stacks of the  
512 Fe-Mn factory, especially from the stack above the firing area, with a toluene/benzene ratio in  
513 the range 2-3. However, during NE wind periods, the toluene/benzene ratio was always  $\sim 0.5$   
514 at the sampling site, similar to the ratio previously measured in the same area (Roukos et al.,



515 2009). This result implies either that emissions from the stacks were already highly processed  
516 when the plumes reached the sampling site (as evidenced previously for particles), or that  
517 there was another important source of benzene near the Fe-Mn plant (e.g. the steelworks,  
518 Ciaparra et al., 2009). Several additional events were identified, such as during the nights of  
519 May 22-23, May 23-24, and May 31-June 1, with an increase of short-chain alkanes (Figure  
520 5g). These events took place during NW and W wind periods, suggesting that short-chain  
521 alkane emissions could possibly be related to petrochemical industrial activities in the area  
522 (Figure 1a).

523 On the bottom right of Figure 5, two pie charts show the average VOC composition during  
524 NE wind periods (downwind metalworking sources) and measured at the stacks. VOCs  
525 emitted at the stacks are totally dominated by aromatic compounds (mainly toluene and  
526 benzene), which account for 60% of the total measured VOCs, while this class of compounds  
527 accounts for only 31% at the sampling site during NE wind periods. These pie charts also  
528 show that oxygenated compounds emitted at the stacks represent 7% of the total VOCs, while  
529 at the sampling site, they account for 27% of the total VOCs. Moreover, none of the  
530 oxygenated compounds identified at the sampling site come from aromatic precursors. These  
531 results suggest that emissions from the stacks are, during NE wind periods, quickly diluted in  
532 an aged air mass before reaching the sampling site. This also confirms previous observations  
533 within the same industrial complex (Roukos et al., 2009) that highlighted the fact that even in  
534 anthropogenically-influenced areas, long-range transport can have a significant contribution  
535 to the observed concentrations of gaseous pollutants.

536 Figure 5d-e shows the time series of the main trace gases (CO, CO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, SO<sub>2</sub>). Among  
537 them, CO<sub>2</sub> and O<sub>3</sub> were the only gases to show significant diurnal trends. O<sub>3</sub> varied between  
538 20 ppb (nighttime) and 40 ppb (daytime) on average. The average CO<sub>2</sub> concentration was 460

539 ppm during the night and 430 ppm during the day. Its diurnal pattern was mainly driven by  
540 boundary layer dynamics. Vegetation and variation in the surface temperature of the sea could  
541 also influence the diurnal pattern of CO<sub>2</sub>. The concentration of the other gases varied  
542 dynamically throughout the study. CO and SO<sub>2</sub> increased significantly during NE wind  
543 periods, when the sampling site was under the direct influence of metallurgical emissions.  
544 The CO concentration during these periods was in the range 3-10 ppm, ~10 times higher than  
545 during other periods. The SO<sub>2</sub> concentration also increased 10-fold during NE wind periods.  
546 Measurements performed at the stacks of the Fe-Mn factory confirmed that the firing area of  
547 the sintering unit of the plant emitted very large amounts of these two gases (Table 2).  
548 Sulfuric acid is one species commonly involved in particle nucleation, along with water  
549 (Holmes, 2007; Zhang et al., 2012). Therefore, the very high amounts of SO<sub>2</sub> emitted by this  
550 factory, followed by its rapid oxidation to sulfuric acid, could play a major role in the new  
551 particle formation events observed at the sampling site downwind of metalworking emissions  
552 (Section 4.2). However, for the period of sea breezes during which the sampling site was  
553 unambiguously influenced by metalworking plumes (Figure 4b and 4d), organics in NR-PM<sub>1</sub>  
554 are clearly more abundant than sulfates (Figure 4e). Thus, after the formation of new particles,  
555 which have a diameter of a few nm, the growth of these particles up to larger sizes could be  
556 more driven by organics than by sulfate formation, or results from fast agglomeration  
557 processes with preexisting particles.

#### 558 **4.4 Physico-chemical characteristics of plumes influenced by different pollutant** 559 **sources**

560 Considering the atmospheric dynamic from LIDAR and SODAR data (section 3), three short  
561 time (30 minutes) but highly specific events were identified, influenced by steelworks and Fe-

562 Mn plant activities (from NE-E wind direction), by petrochemical activity (from NW wind  
563 direction) and by urban activities (from SE wind direction), respectively. The corresponding  
564 gas and particle parameters are listed in Table 2, while Figure 9 shows the average particle  
565 number size distributions during these three thirty-minute periods. The particle ( $PM_{2.5}$ , sum  
566 NR- $PM_1$  and particles number concentrations) and gas ( $CO$ ,  $SO_2$ ) concentrations were very  
567 high in the metalworking emissions. Indeed, the total NR- $PM_1$  concentration in this plume  
568 was  $37.7 \mu g m^{-3}$ , much higher than in the plume from the refinery in the NW ( $16.2 \mu g m^{-3}$ )  
569 and from the urban traffic in the S ( $2.9 \mu g m^{-3}$ ), while the particle number concentration was  
570 around 20-30 times higher. In terms of chemical composition, the contributions of nitrate  
571 (22.3%, vs. 12.3% for petrochemistry and 13.8% for urban emissions) and non-sea salt  
572 chloride (6.9%, vs. 1.2% and 3.4%) were significantly higher, and that of sulfate lower  
573 (12.7%, vs. 50.0% and 24.1%) in the plume from the metallurgy plant and steelworks,  
574 compared to the two other plumes. Results obtained with the ATOFMS (Table 2) showed that  
575 most metal-containing particles were also mainly coming from the metallurgical area, such as  
576 Fe- and K-rich particles. In addition to these, Ca, Pb, and other metals-rich particles were also  
577 present in much higher concentrations when the near-field site was under the influence of  
578 metallurgical emissions. Among the trace gases,  $CO$  and  $SO_2$  were significantly higher during  
579 the NE-E wind period, compared to other periods, and thus their presence was highly  
580 influenced by these industrial activities. The presence of high mixing ratios of  $SO_2$  (47.8 ppb),  
581 and low contributions of sulfate during the NE-E wind period suggest that chemical  
582 processing was not fast enough to totally oxidize  $SO_2$  to sulfate over a distance of  $<1$  km,  
583 even if new particle formation events were observed at the sampling site during this NE-E  
584 wind period (see Section 4.3). However, considering metal-bearing particles as a proxy for  
585 refractory compounds, the latter contribution to particles smaller than 100 nm is relatively low

586 during NE wind periods (Figure 6, May 23-25 and May 25-27 samples). This size fraction is  
587 then probably dominated by the non-refractory fraction, and notably by organic compounds  
588 which account for 45 % of NR-PM<sub>1</sub> concentration during the plume from the NE-E (Table 2).  
589 This result strongly suggests that after the formation of new particles in the plume from the  
590 metallurgical area, their growth to larger sizes was largely driven by the condensation of  
591 organics.

592

## 593 **5 Conclusion**

594 The aim of the NANO-INDUS project was to study the evolution of physico-chemical  
595 characteristics of fine particles emitted by industrial activities over a short distance, before  
596 they reach surrounding populated areas. This was performed in two steps. First, particles  
597 emitted by a ferromanganese alloy plant, located in a multi-influenced industrial area, were  
598 directly sampled and analyzed. Secondly, a field campaign was undertaken in the near-field of  
599 the plant chimneys, in order to determine the concentration, chemical composition, and size  
600 distribution of the fine particles emitted in this multifaceted atmospheric environment.

601 Results obtained during the field campaign showed that unstable atmospheric conditions  
602 inside the thermal internal boundary layer (TIBL), due to the occurrence of sea breezes,  
603 promote entrapment and mix of pollutants (here Fe-Mn plant emissions, mixed with  
604 emissions from an adjacent steelworks). These TIBL unstable periods were characterized by a  
605 very high mass concentration of fine particles ( $38 \mu\text{g m}^{-3}$  NR-PM<sub>1</sub>), compared to other  
606 periods dominated by urban or marine influences. These results highlight the huge influence  
607 of metalworking emissions on ambient air quality and raise questions about occupational  
608 exposure of workers. The chemical composition of particles during these sea breeze periods

609 was also characteristic, as the contribution of metal-rich particles, organics, and nitrates  
610 increased significantly, while that of sulfate decreased, compared to other periods. In addition  
611 to new particle formation at the stacks of the Fe-Mn plant, particle growth was also observed  
612 in the plume from the metallurgical area. In parallel to possible fast agglomeration processes  
613 with preexisting particles, the latter phenomenon was mainly driven by the condensation of  
614 organics.

615 This work has important implications in terms of air quality monitoring strategies. First,  
616 people working in an industrial area may be continuously exposed to fine particle  
617 concentrations going well beyond recommendations from Public Health Authorities (e.g. the  
618 WHO annual mean guideline value of  $10 \mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$ ). Second, our results show that,  
619 even over short distances, the chemical composition and size of these fine particles may  
620 evolve rapidly, and that their characteristics at the boundary of an industrial complex may  
621 differ from those directly emitted at the stacks, the only position monitored by manufacturers  
622 to comply with regulation and develop emission control strategies. Generally speaking, it is  
623 therefore suggested, for towns increasingly influenced by such activities, that air quality  
624 management plans address these observations, for example by means of special monitoring in  
625 neighboring urban zones, dedicated to the apportionment of processed metalworking  
626 emissions.

627

#### 628 **Author contribution**

629 PF, NL, KD, VR, LYA, CS, and JCW designed the study. AS, PF, NL, KD, VR, LYA, and  
630 CS organized the field campaign at the Fe-Mn plant. AS, PF, NL, KD, VR, LYA, CS, JA, PA,  
631 RMH, FC, DD, PD, MF, PG, TL, HM, and SM participated in the data acquisition during the

632 field campaign and worked on the data treatment. All the co-authors participated in the  
633 interpretation of the results. AS wrote the manuscript, with contributions from PA and MF for  
634 the sections on atmospheric dynamics and metalworking plume detection. All the co-authors  
635 gave their feedback on the different versions of the manuscript, and approved the final  
636 version.

637

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647

### 648 **Declarations of interest**

649 None.

650

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857 **Table 1.** List of selected elemental ratios for the stacks and the sampling site (data from  
 858 ICP/MS and ICP/AES analyses).

		Mn/Fe	Mn/Al	Fe/Ca	Na/Mg	V/Ni	Zn/Pb	Cu/Sb	Pb/Cd
Stacks	Firing area (A)	2.62	2.99	0.91	<DL	0.34	0.07	12.2	15.0
	Cooling area (B)	3.34	3.59	4.19	<DL	0.53	0.51	70.0	21.3
	Smelting unit (C)	0.46	1.25	2.86	2.47	0.00	11.9	<DL	46.3
Sampling site	15-17/5	0.67	0.86	0.70	2.23	0.62	1.03	10.2	36.6
	17-19/5	0.26	0.34	1.07	0.43	0.19	5.56	10.4	31.3
	19-21/5	1.90	1.29	1.43	1.09	0.88	2.32	15.8	13.5
	21-23/5	0.59	0.24	0.61	1.92	1.01	2.00	3.15	35.7
	23-25/5	0.58	0.75	0.92	5.18	1.17	2.31	8.77	29.8
	25-27/5	0.30	1.51	1.86	2.17	1.08	3.19	11.1	19.5
	27-29/5	0.28	0.66	1.61	6.27	1.20	2.83	7.21	26.3
	29-31/5	0.73	0.43	0.43	0.35	1.12	1.52	3.55	37.7
	31/5-1/6	1.19	0.55	0.46	0.81	0.72	3.61	3.19	31.6
	1-3/6	0.39	1.29	1.48	3.43	0.79	3.48	13.2	42.2
	3-5/6	0.45	0.30	1.00	0.85	0.45	2.11	7.62	56.4
	5-6/6	0.96	0.07	0.34	0.00	0.05	4.74	2.61	15.7
	Average	0.69	0.69	0.99	2.06	0.77	2.89	8.06	31.4
	Std dev	0.47	0.46	0.51	1.98	0.38	1.31	4.31	11.9
	Median	0.59	0.61	0.96	1.51	0.84	2.58	8.20	31.5
Min	0.26	0.07	0.34	0.00	0.05	1.03	2.61	13.5	
Max	1.90	1.51	1.86	6.27	1.20	5.56	15.8	56.4	

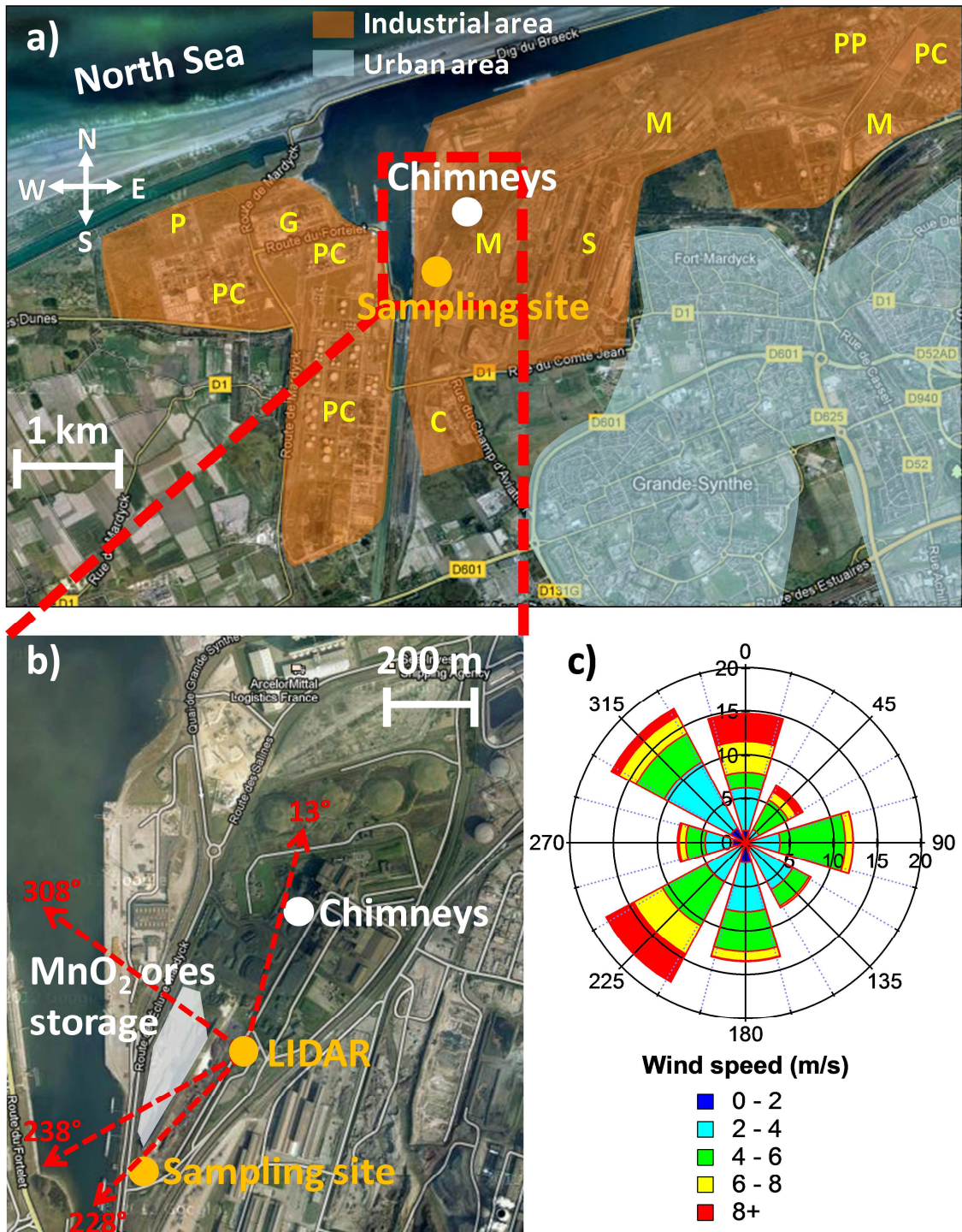
859 DL: Detection Limit

860 **Table 2.** Summary of meteorological conditions and concentrations of particle- and gas-phase  
 861 data during specific plumes reaching the sampling site and identified with the LIDAR and  
 862 SODAR.

	Wind direction	NE-E	NW	SE
	Plumes	Steelworks Fe-Mn plant	Petrochemistry	Urban
	Date	26/05/2012	03/06/2012	07/06/2012
	Start time (UTC)	10:15 am	11:30 am	5:30 am
	End time (UTC)	10:45 am	12:00 pm	6:00 am
Weather station	Temperature [°C]	21.3	11.8	15.6
	Relative humidity [%]	55	94	87
	Solar radiation [W m <sup>-2</sup> ]	801	51	90
Sonic anemometer	Wind speed [m s <sup>-1</sup> ]	4.4	2.8	3.4
	Atmosphere	unstable	very unstable	unstable
Beta Gauge	PM <sub>2.5</sub> [µg m <sup>-3</sup> ]	65.7	N/A	4.5
SMPS	Particle number [# /cm <sup>3</sup> ]	154'847	5'809	7'446
HR-ToF-AMS	Org [µg m <sup>-3</sup> ]	16.8	2.4	1.3
	SO <sub>4</sub> <sup>2-</sup> [µg m <sup>-3</sup> ]	4.8	8.1	0.7
	NO <sub>3</sub> <sup>-</sup> [µg m <sup>-3</sup> ]	8.4	2.0	0.4
	NH <sub>4</sub> <sup>+</sup> [µg m <sup>-3</sup> ]	5.1	3.5	0.4
	Cl [µg m <sup>-3</sup> ]	2.6	0.2	0.1
	Sum NR-PM <sub>1</sub> [µg m <sup>-3</sup> ]	37.7	16.2	2.9
Aethalometer	BC [µg m <sup>-3</sup> ]	1.3	0.4	1.0
ATOFMS	Na-rich [count hr <sup>-1</sup> ]	27	44	224
	K-rich [count hr <sup>-1</sup> ]	275	89	31
	EC [count hr <sup>-1</sup> ]	75	274	35
	OC & PAH [count hr <sup>-1</sup> ]	6	8	8
	Fe-rich [count hr <sup>-1</sup> ]	67	58	8
	Ca-rich [count hr <sup>-1</sup> ]	25	13	10
	Mn-rich [count hr <sup>-1</sup> ]	10	11	5
	Pb-rich [count hr <sup>-1</sup> ]	23	14	0
	V-rich [count hr <sup>-1</sup> ]	2	3	0
Others [count hr <sup>-1</sup> ]	220	6	12	
VOCs cartridges, TD-GC/MS	Biogenic VOCs [µg m <sup>-3</sup> ]	1.8	0.8	0.6
	Aromatics [µg m <sup>-3</sup> ]	9.1	5.7	1.5
	Alkanes [µg m <sup>-3</sup> ]	7.7	17.7	2.0
	Alkenes [µg m <sup>-3</sup> ]	8.7	3.2	2.5
	Oxygenated VOCs [µg m <sup>-3</sup> ]	11.5	6.2	3.9
Gas analyzers	CO [ppb]	4666	363	692
	NO <sub>x</sub> [ppb]	N/A	15.7	12.8
	O <sub>3</sub> [ppb]	17.6	16.7	7.2
	SO <sub>2</sub> [ppb]	47.8	N/A	6.6

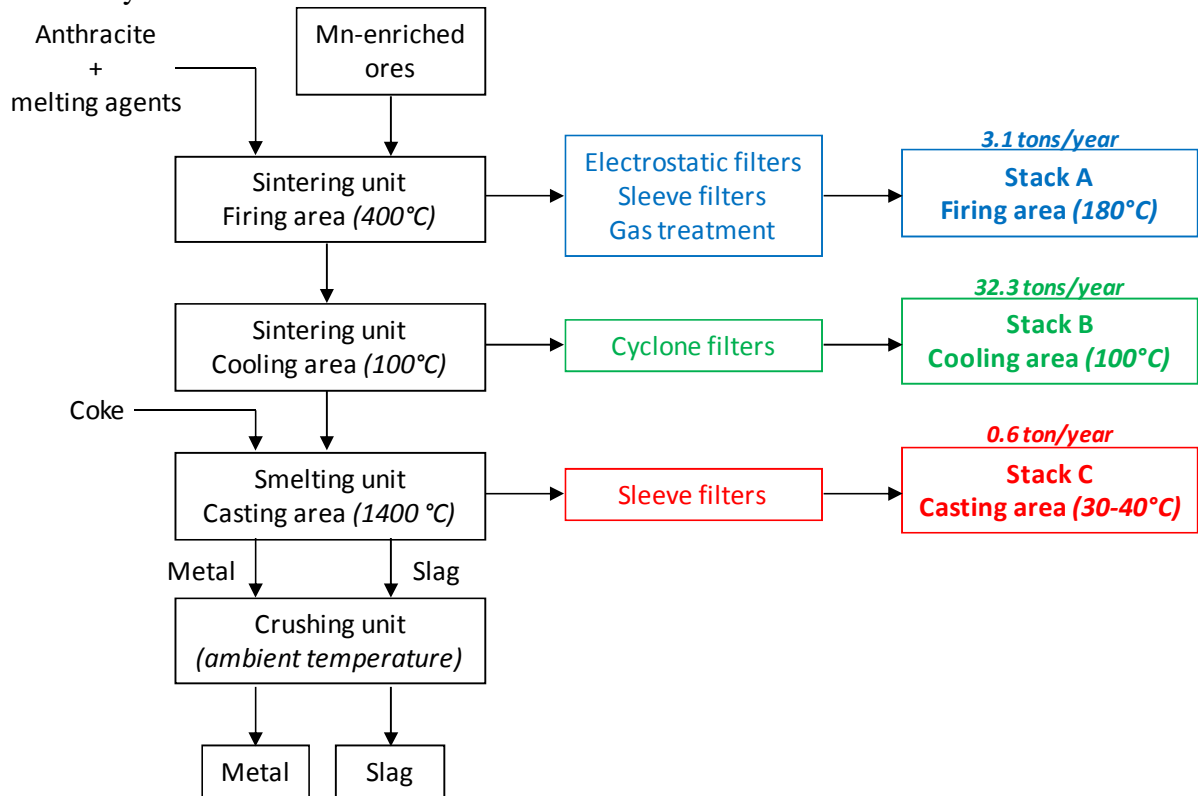
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864 **Figure 1.** (a) Map of the industrial area near Grande-Synthe, with the locations of the  
 865 sampling site, the emission chimneys of the ferromanganese alloy manufacturing plant, and  
 866 other industries. (b) Enlarged map showing the location of the LIDAR, with the four  
 867 directions scanned by the instrument every 15 minutes. (c) Wind rose plot for the entire  
 868 campaign. Key: C chemical plant; G glass manufacturing factory; M metallurgy; P plastic  
 869 manufacturing plant; PC petrochemistry; PP power plant; S steelworks.



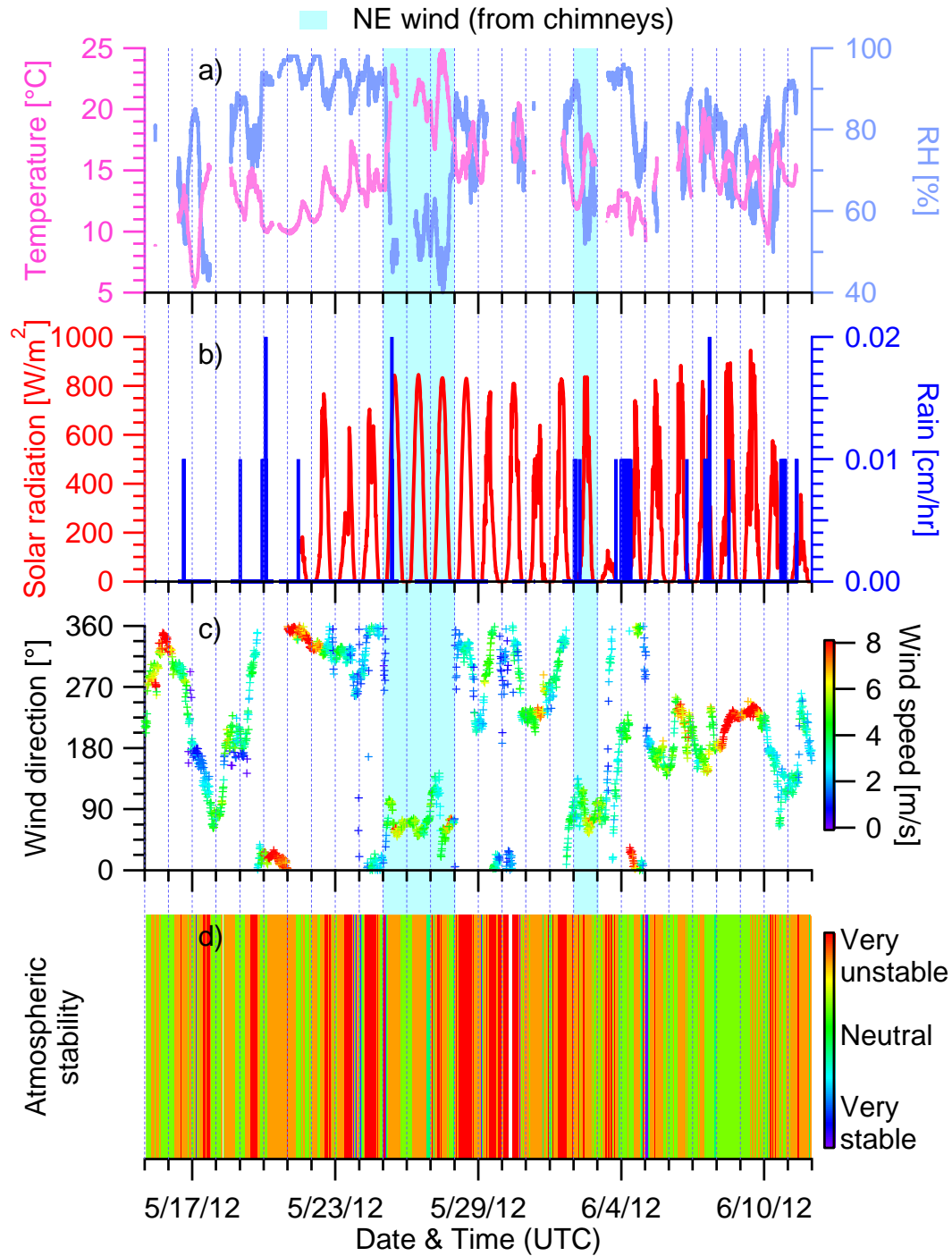
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872 **Figure 2.** Schematic drawing of the ferromanganese alloy manufacturing process and the  
873 filtration system used for each stack.



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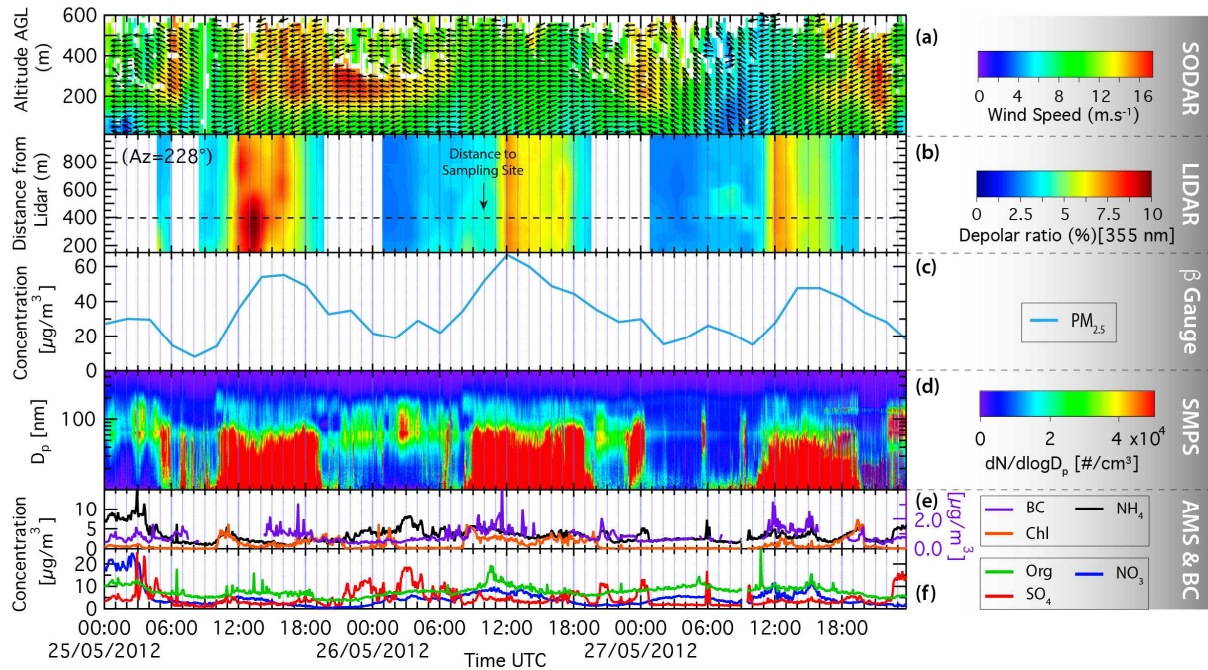
876 **Figure 3:** Time series of (a) temperature and relative humidity, (b) solar radiation and rain, (c)  
877 wind direction colored by wind speed, and (d) atmospheric stability.



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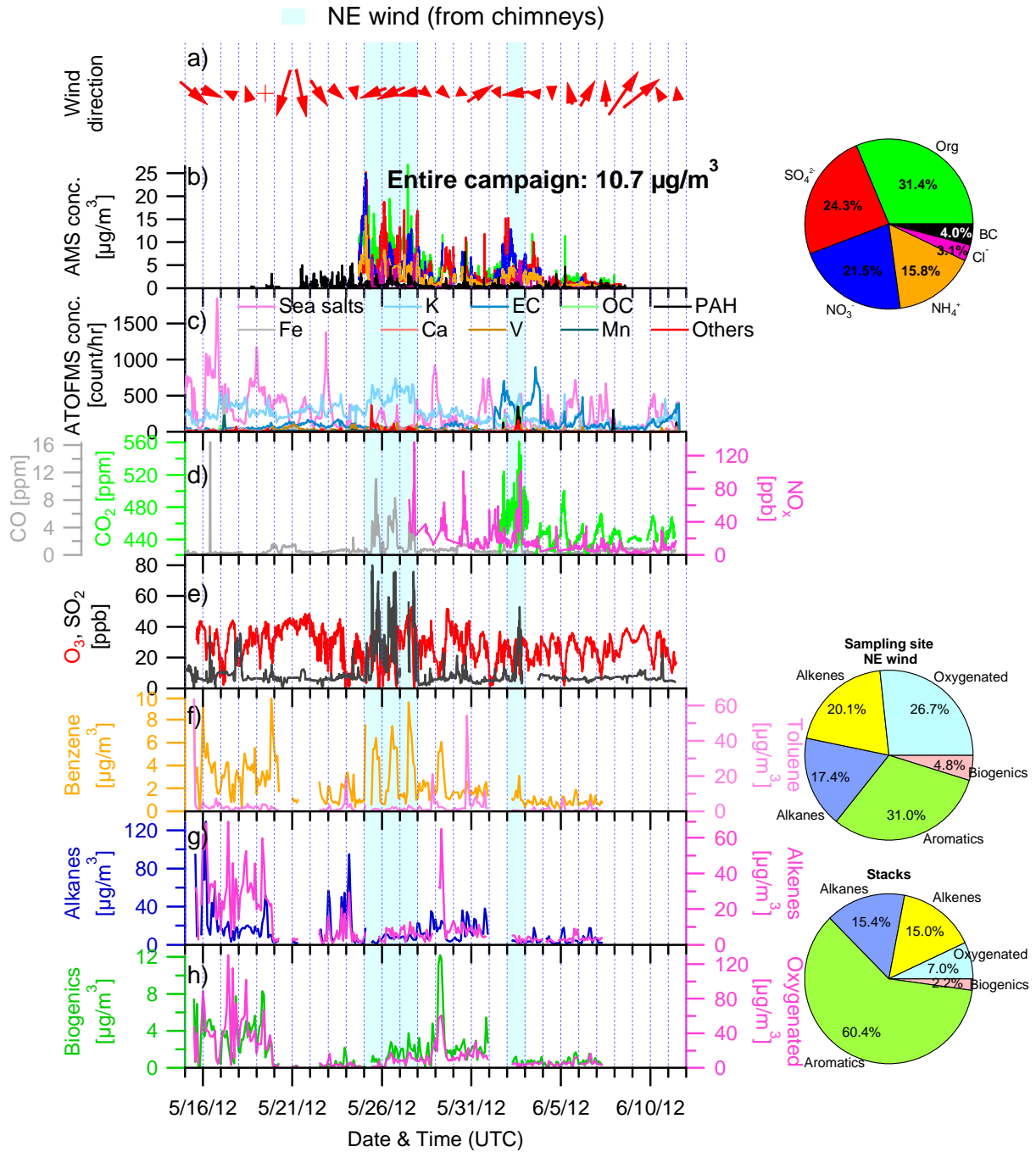


880 **Figure 4.** (a) Time-height section of wind direction and wind speed (from SODAR). (b)  
 881 Time-distance section of the depolarization ratio of LIDAR at 355 nm when the instrument  
 882 was pointed towards the near-field sampling site (azimuth angle 228° in Figure 1b). Time  
 883 series of (c) PM<sub>2.5</sub> (from beta gauge), (d) particle number size distribution (from SMPS), (e)  
 884 ammonium, chloride (from AMS), and BC (from Aethalometer), (f) organics, sulfate, and  
 885 nitrate (from AMS) between May 25<sup>th</sup> and May 27<sup>th</sup>, 2012. The three sea breeze periods are  
 886 shown on the top of the graph.



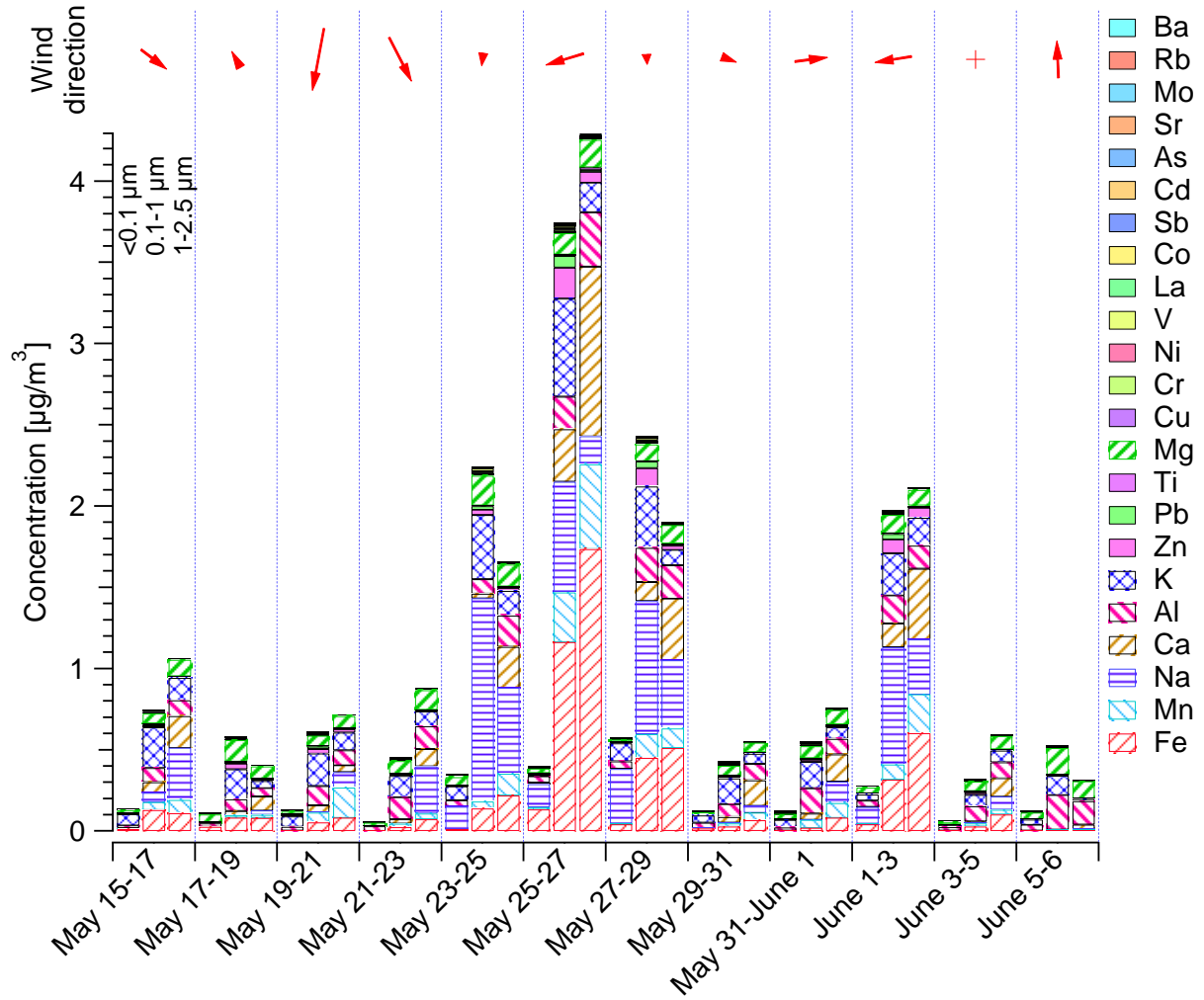
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889 **Figure 5.** Time series of (a) the daily average wind direction (with length of arrows  
 890 proportional to the wind speed), (b) chemical species measured by the AMS, the  
 891 Aethalometer, and (c) the ATOFMS, (d) CO, CO<sub>2</sub>, and NO<sub>x</sub>, (e) O<sub>3</sub> and SO<sub>2</sub>, (f) benzene and  
 892 toluene, (g) alkanes and alkenes, (h) biogenic and oxygenated VOCs. Shaded regions  
 893 correspond to NE wind periods (from stacks). The pie charts show the average contribution  
 894 of the species to the total PM<sub>1</sub> mass and VOCs.



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897 **Figure 6.** Time series of the size-resolved elemental composition (data from ICP/MS and  
 898 ICP/AES analyses of Teflon filters), along with the average wind direction (length of arrows  
 899 are proportional to wind speed).



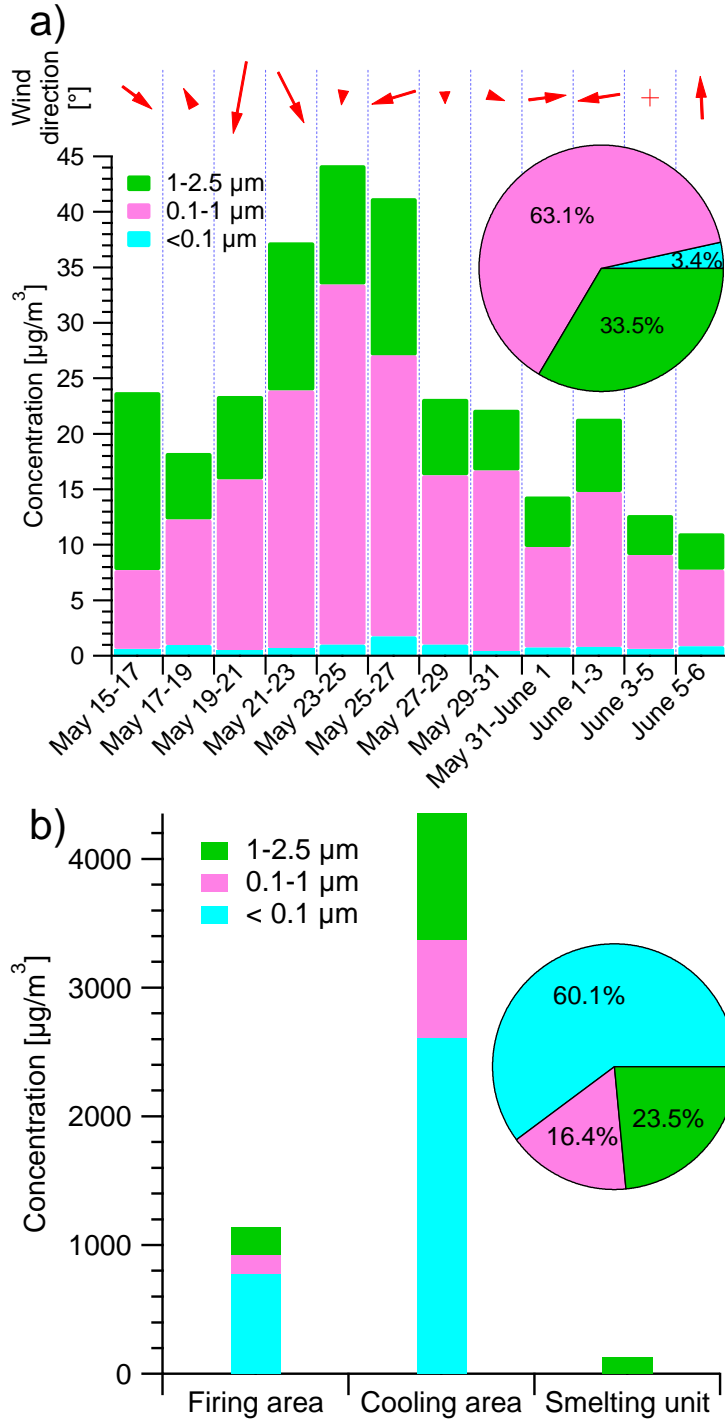
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902 **Figure 7.** (a) Time series of mass size distributions at the near-field sampling site and average wind directions, and (b) average mass size distributions at the stacks of the ferromanganese alloy manufacturing plant (gravimetrically determined from 13-stage impactor filters). Sizes of arrows are proportional to the wind speed.

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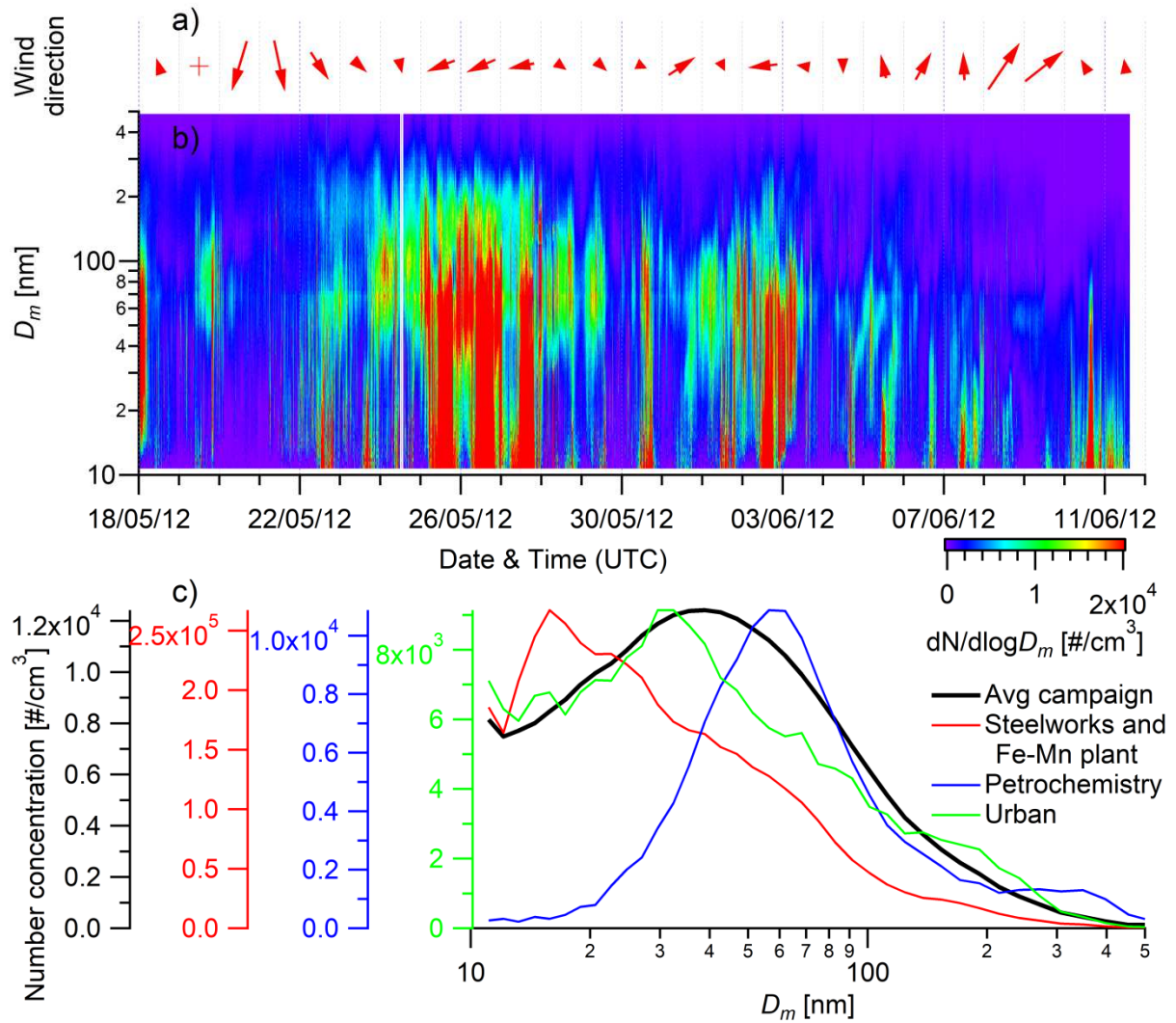
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908 **Figure 8.** Time series of (a) the daily averaged wind direction (with length of arrows  
 909 proportional to wind speed) and (b) the particle number size distribution. (c) Average size  
 910 distributions for the entire campaign and during periods of steelworks + Fe-Mn plant,  
 911 petrochemistry and urban influences (details of the periods in Table 2) (data from the SMPS).



912