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Dall'Osto, Manuel; Beddows, David; Harrison, Roy; Onat, Burcu

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Article

**FINE IRON AEROSOLS ARE INTERNALLY MIXED WITH
NITRATE IN THE URBAN EUROPEAN ATMOSPHERE**

Manuel Dall'Osto, David C.S. Beddows, Roy Michael Harrison, and Burcu Onat

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9 **M. Dall'Osto^{1*}, D.C.S. Beddows², Roy M. Harrison^{2†}**
10 **and Burcu Onat³**
11
12
13

14 **¹Departament de Biologia Marina i Oceanografia**
15 **Institut de Ciències del Mar, CSIC**
16 **Pg. Marítim de la Barceloneta, 37-49**
17 **08003 Barcelona, Catalonia, Spain**
18

19 **²Division of Environmental Health and Risk Management**
20 **School of Geography, Earth and Environmental Sciences**
21 **University of Birmingham, Edgbaston, Birmingham, B15 2TT**
22 **United Kingdom**
23

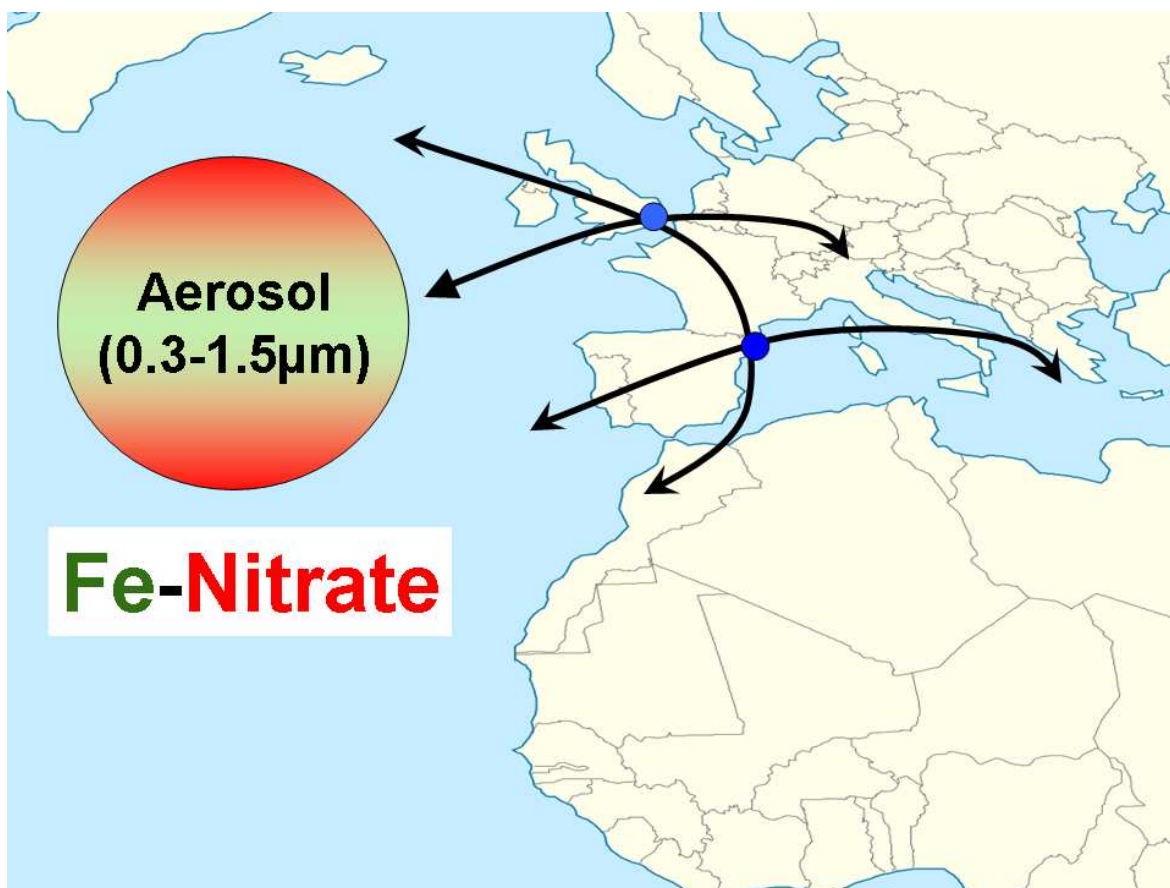
24 **³Istanbul University**
25 **Environmental Engineering Department**
26 **Avcilar 34320, Istanbul, Turkey**
27
28
29
30
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32

* To whom correspondence should be addressed. Tele: +34 0044 644 053 801; Email: dallosto@icm.csic.es

† Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

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37 **ABSTRACT**

38 Atmospheric iron aerosol is a bioavailable essential nutrient playing a role in oceanic productivity.
39 Using Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS), the particle size (0.3-1.5 μm),
40 chemical composition and mixing state of Fe-containing particles collected at two European urban
41 sites (London and Barcelona) were characterised. Out of the six particle types accounting for the
42 entire Fe-aerosol population, that arising from long range transport (LRT) of fine Fe-containing
43 particles (Fe-LRT, 54-82% across the two sites) was predominant. This particle type was found to
44 be internally mixed with nitrate and not with sulphate, and likely mostly associated with urban
45 traffic activities. This is in profound contrast with previous studies carried out in Asia, where the
46 majority of iron-containing particles are mixed with sulphate and are of coal combustion origin.
47 Other minor fine iron aerosol sources included mineral dust (8-11%), traffic brake wear material (1-
48 17%), shipping/oil (1-6%), biomass combustion (4-13%) and vegetative debris (1-3%). Overall -
49 relative to anthropogenic Asian Fe-sulphate dust - anthropogenic European dust internally mixed
50 with additional key nutrients such as nitrate is likely to play a different role in ocean global
51 biogeochemical cycles.

52

53

54

55 **Keywords:** Iron particles; mineral dust; non-exhaust; nitrate; ATOFMS

56

57 **1. INTRODUCTION**

58 Atmospheric particulate matter (PM) has well known adverse effects on human health¹ and
59 atmospheric visibility; and partly compensates climate forcing by greenhouse gases.² Iron (Fe) is a
60 major element found in the atmospheric aerosol. Atmospheric Fe has both natural (e.g. aeolian
61 desert dust transport) and anthropogenic (e.g. iron/steel and general industrial activities, traffic)
62 origins.^{3,4} Coarse particles (PM_{2.5-10}) are often considered to be related to crustal elements and
63 resuspension of road dust.⁴ However - within the urban environment - Harrison et al.⁵ found that the
64 iron concentration within coarse dusts was much greater at roadside sites than at urban background
65 sites and this was considered indicative of road traffic and most probably the vehicles themselves as
66 a source. Gietl et al.⁶ also showed that Fe and other brake wear elements (Cu, Ba, Sb) have very
67 similar particle size distributions at a roadside site, implying a common source. Dall'Osto et al.⁷
68 found that Fe and Cu together can also be used as a tracer of brake wear also in PM_{2.5} aerosol
69 sampled in the urban agglomerate of Barcelona (Spain).

70

71 In general little is known about aerosol sources of Fe-containing particles in the finer mode (PM₁)⁸⁻
72 ⁹⁻¹⁰ in the urban atmosphere. Although fine aerosol modes contribute little Fe to the total aerosol
73 mass, it has much greater potential for respiratory intake, and its involvement in health effects. Fe is
74 a transition metal which is considered to exert toxic effects, which may release free radicals in lung
75 tissues via the Fenton reaction, and are hypothesized to cause cellular inflammation.^{11,12} Iron
76 aerosol particle size influences their reactivity, toxicity and solubility.¹³ Since particle-bound metals
77 need to dissolve and become free ions in the lung fluid, particle solubility is considered a major
78 criterion for the bioavailability and therefore toxicity.^{12,14} Atmospheric Fe may be associated with
79 adverse health effects due to mechanisms such as DNA strand breakage and tissue or cell damage.¹⁵

80

81 Fine Fe plays a role also in ocean/climate biogeochemical cycles, and it might actually be more
82 important than coarse Fe-containing aerosol^{16,17}. Briefly, iron is an essential nutrient for all

83 organisms, used in a variety of enzyme systems, including those for photosynthesis, respiration, and
84 nitrogen fixation.¹⁶ Several studies have argued that the greater solubility at lower dust mass
85 concentration could be due to a larger surface area to volume ratio of the finer dust particles.¹⁷⁻¹⁹
86 However, the size dependence of the fractional Fe solubility (FFS) can at most explain a small part
87 of the measured variability in FFS in atmospheric aerosol samples. The high values of the FFS of >
88 1% in atmospheric aerosol samples are related to a number of atmospheric processes and natural
89 and anthropogenic sources and are clearly not well understood.¹⁷ It is also important to keep in
90 mind that although combustion sources are not important for the total Fe mass compared to natural
91 sources, they can contribute up to 50% of soluble Fe deposited into oceanic regions²⁰⁻²¹. Overall, the
92 relationships between iron solubility, oxidation state, and bioavailability are complex and poorly
93 understood.

94

95 Evidence for the importance of such a dust–ocean–climate feedback process is still limited. Whilst
96 the role of desert dust is currently being studied¹⁷⁻²⁰, far less information is available on Fe-
97 containing urban anthropogenic dust²². Urban influenced air masses can travel long distances.
98 Continental polar air masses originating in Europe travel southwards across the Mediterranean,
99 North Africa and finally reach the tropical Atlantic Ocean²³. Continental polar air masses
100 originating in Portugal and Ireland also travel southwards to the Canary Island waters²⁴. Northern
101 European air masses originating in the continent of Europe can travel across the British Isles and
102 further to the North Atlantic Ocean. For example, results from Mace Head (Ireland) show that these
103 continental polar air masses travel to the Atlantic Ocean fairly often, about a third of the time²⁵⁻²⁶.
104 Once urban anthropogenic dust is deposited in the ocean, its impact on marine productivity will
105 depend on a number of factors, including the bioavailability of the chemical components present in
106 the dust^{3,27,28}.

107

108 In order to characterise the sources, transport and transformations of Fe aerosols in the atmosphere,
109 a comprehensive approach that simultaneously characterises single particles for aerodynamic
110 diameter and chemical composition is needed²⁹. The use of single-particle analysis is an important
111 analytical tool because it allows determination of how the chemical constituents are distributed
112 between individual particles (mixing state). Specifically, in this work we are interested in
113 apportioning which secondary chemical components (i.e. nitrate, sulphate) are mixed within Fe
114 containing aerosols; because this can have implications for solubility and additional nutrient
115 capability³⁰⁻³². We use Aerosol Time-of-Flight Mass Spectrometry (ATOFMS), which provides
116 information on the abundance of different types of aerosol particles as a function of particle size
117 with a much high time resolution and better count statistics²⁹. For the purpose of our work, the
118 ATOFMS is more suitable than other single particle techniques. For example, Transmission
119 electron microscopy (TEM) is a powerful technique capable of simultaneously obtaining unique
120 information on individual particles regarding metal speciation, size, mixing state, and
121 morphology³³⁻³⁴. However, semi-volatile particle types (i.e. nitrate) are liable to vaporise in the high
122 vacuum environment of the TEM and therefore not be observed³⁵.

123

124 A few specific studies reporting the sources and mixing state of iron-containing particles can be
125 found in the literature. Furutani et al.³⁶ utilized single particle mass spectrometry to classify Fe-
126 containing particles based on their chemical associations. Fe-containing particles have numerous
127 sources, especially anthropogenic sources such as coal combustion. Indeed, mineral dust was found
128 to be a minor contributor to the total iron concentration, whereas the importance of the coal
129 combustion source in East Asia was emphasised. Complementary measurements^{21,36} performed at
130 the same time and location¹⁸ showed that field-collected atmospheric Fe-containing particles were
131 found to be internally mixed with secondary species such as sulfate, soot, and organic carbon.
132 Recently, Zhang et al.³⁷ showed ATOFMS results collected in Shanghai (China) for nearly 22 d
133 during the winter of 2011. Fe-containing particles were mainly clustered into four chemical groups,

134 comprising Fe-rich, K-rich, Dust and V-containing particle types. It was concluded that major
135 sources of Fe-containing particles correspond to various anthropogenic sources including iron/steel
136 industrial activities, and fly ash from both biomass burning and coal combustion, accounting for
137 55% and 18%, respectively. Hu et al.³⁸ also stressed that sources of Fe-bearing particles in the
138 Beijing atmosphere (China) are mainly local steel industries and oil fuel combustion. As a
139 consequence, the majority of the Fe-containing particles collected in Asia are found to be mainly
140 internally mixed with sulphate^{21,36-38}. With regard to other study areas, to our knowledge there are
141 not specific ATOFMS studies on the matter.

142

143 In summary, whilst coarse Fe-containing particles (PM_{2.5-10}) are often associated with mineral dust,
144 road dust and non-exhaust traffic material, little is known of the sources of finer Fe-containing
145 particles. Furthermore, to our knowledge all aerosol mixing state studies on Fe-containing particle
146 studies presented in the literature discuss ambient data collected in Asia. This study reports
147 information on sources and mixing state of Fe-containing particles sampled over the European
148 continent. Both meteorology and emissions show large variations across Europe, and conclusions
149 from a certain region cannot necessarily be extrapolated to other parts of the continent. Latitude
150 variations within Europe influence mineral matter³⁹, Saharan dust intrusion⁴⁰, secondary inorganic
151 aerosol⁴¹ and sea salt concentrations⁴². For this reason, we consider two different ambient ATOFMS
152 datasets from Barcelona (Spain) and London (England). Whilst both monitoring sites are classified
153 as "roadside" sites, the Spanish one presents a minor road in an environment subject to more
154 Saharan dust intrusion in a drier climate.²⁶ By contrast, the monitoring site in London is near a
155 major road under typical North European weather conditions.⁴⁴ We use two road side sites cause we
156 want to apportion both local road traffic²² and regional long range transport sources. Further
157 ATOFMS studies previously published in other background European locations (Mace Head,
158 Ireland; Po Valley, Italy and Port Talbot, Wales) are also compared with the presented results.
159 Different aerosol sources are inferred and discussed, including their average aerosol sizes and

160 mixing state. An important comparison with existing ATOFMS data collected in Asia is also
161 presented, and its implication for marine biogeochemistry discussed.

162

163 **2. METHODS**

164 **2.1 Locations**

165 This study aimed to elucidate the Fe-containing aerosol sources and their mixing state in two
166 different European cities. The first was London - which has a population of 7.6 million, whilst the
167 Greater London metropolitan area has between 12.3 and 13.9 million, making it the largest in the
168 European Union.⁴⁵ The sampling campaign was conducted at Marylebone Road (51.52°N, 0.15°W),
169 a six-lane heavily trafficked road within an urban canyon, between 22nd May and 11th June 2009.
170 Instruments were installed in a permanent monitoring station located at kerbside, 1m from the busy
171 six-lane highway, Marylebone Road, carrying ca 80,000 vehicles per day. Inlets were sited about 3
172 m above ground level (a.g.l.) at differing distances from the road, mostly 1–3 m distant. The second
173 city was Barcelona, capital of Catalonia, a large coastal urban agglomerate located in the Western
174 Mediterranean Basin in the north-east (NE) part of Spain. The sampling campaign (SAPUSS,
175 Solving Aerosol Problems by Using Synergistic Strategies)⁴² took part in Barcelona between 20th
176 September and 20th October 2010 (local time, UTC+2). The Road site (lat 41.388423; lon
177 2.150213) was situated in a car park next to a major road (Carrer Urgell). The road, which cuts the
178 city from South East to North West, is a street canyon composed by a two-way cycle path and a
179 one-way four lane vehicle road. Vehicle intensity for the month of measurements was about 17,000
180 vehicles per day. Air was drawn from outside the instruments throughout a number of home-
181 designed inlets, situated on the vans' roofs at a height of about 4m above ground with 1/4 inch
182 stainless steel tube led inside each trailer (length about 2 m) to a manifold.

183 With regard to air mass back trajectory analysis run for the two ambient field campaigns herein
184 presented, it was shown in previous studies that air masses travelling over the study areas continue

185 to travel and reach nearby and far oceans and seas about a quarter of the ambient field study
186 time^{43,46}

187

188 **2.2 Instrumentation**

189 Since its introduction in the late 1990s, the ATOFMS has given valuable insights into the size and
190 composition of individual airborne particles.^{47,48} The ATOFMS (Model 3800-100, TSI, Inc.)
191 collects bipolar mass spectra of individual aerosol particles. Ambient aerosol is focused into a
192 narrow particle beam for sizes between 100 nm and 3 μm . Using a 2-laser velocimeter, particle
193 sizes are determined from particle velocity after acceleration into the vacuum. In addition, the light
194 scattered by the particles is used to trigger a pulsed high power desorption and ionization laser
195 which evaporates and ionizes the particle in the centre of the ion source of a bipolar reflectron ToF-
196 MS. Thus, a positive and a negative ion spectrum of a single particle are obtained. The mass
197 spectrum is qualitative in that the intensities of the mass spectral peaks are not directly proportional
198 to the component mass but are dependent on the particle matrix, the coupling between the laser and
199 the particle and the shot to shot variability of the laser. However, the ATOFMS can provide
200 quantitative information on particle number as a function of composition; providing a measure of all
201 particle components and can be used to assess mixing state.

202

203 Depending on the scientific objectives, past studies have typically used the aerodynamic lens
204 system to study ultrafine and fine anthropogenic emissions⁴⁹ or the nozzle orifice system to study
205 dust particles.²¹ In this study we focus on fine aerosol, so we chose the aerodynamic lens system
206 configuration for better count statistics. Additionally, it is important to note that this study uses the
207 same ATOFMS aerodynamic lens configuration used in past ATOFMS studies characterising Fe-
208 containing particles in Asia.^{21,36,37}

209

210 Fe-containing particles commonly produce an intense ion peak at mass-to-charge ratio (m/z) 56 in
211 the positive ion mass spectrum. As discussed in Zhang et al.³⁷, simply using the ion peak at m/z 56
212 as a unique marker for Fe is not suitable, since it might also be caused by the presence of CaO^+ ,
213 KOH^+ , or $\text{C}_3\text{H}_4\text{O}^+$ from other components. There are also other contributors (mainly organic) at
214 $m/z = 54$. Therefore, as previously described^{36,37} the natural isotopic composition of Fe ($^{54}\text{Fe}/^{56}\text{Fe}$)
215 was adopted as a basis for the Fe screening process to minimize the interference from other species.
216 A peak-area ratio $^{56}\text{Fe}/^{54}\text{Fe} > 10$ was finally applied as recommended by Zhang et al.³⁷ to strengthen
217 the screening through excluding more ambiguous assignments. The screened Fe-containing
218 particles were subsequently imported into YAADA (Yet Another ATOFMS Data Analyzer) and
219 single-particle mass spectra were grouped with adaptive resonance theory neural network, ART-
220 2a.⁵⁰ The parameters used for ART-2a in this experiment were: learning rate 0.05, vigilance factor
221 0.85, and 20 iterations. Further details of the parameters can be found elsewhere.³⁷ An ART-2a area
222 matrix (AM) of a particle cluster represents the average intensity for each m/z for all particles
223 within a group. An ART-2a AM therefore reflects the typical mass spectra of the particles within a
224 group.

225

226 3. RESULTS

227 Overall, 890,873 and 693,462 ATOFMS mass spectra were apportioned in Barcelona⁴³ and
228 London⁴⁶, respectively. The two datasets were merged and the resulting total number of particles
229 (1,584,335) were queried for Fe following the methodology explained in section 2.2, and a total
230 number of 10,549 particles (6,375 in Barcelona, 4,174 in London) were found. By running ART-2a
231 on the combined dataset, more than 300 clusters were found initially but many were merged if they
232 presented similar temporal trends, size distributions and similar mass spectra.⁵¹ By merging similar
233 clusters, the total number of clusters describing the whole database was reduced to six, which are
234 described in the following sub-sections.

235

236 3.1 Regional Fe-Containing Particles from Long Range Transport (Fe-LRT)

237 This was found to be the most frequently occurring cluster (54-82%, Table 1). The average
238 ATOFMS Art-2a cluster (Fig. 1a) shows strong signals at m/z 54 and 56 (^{54}Fe and ^{56}Fe ,
239 respectively) and iron oxide ($[\text{FeOH}]^+$, m/z 73). It is found internally mixed with nitrate (m/z -46
240 and -62 in the negative spectra). This particle type was mainly distributed in the fine mode peaking
241 at around 0.4-0.7 μm in aerodynamic diameter (Fig. 2). In Barcelona, Fe-rich particles were found
242 to correlate with ATOFMS Long Range Transport (LRT) nitrate associated with long range
243 transport of pollutants⁴³. The small mode of this particle type reflects the fact that only fine particles
244 were likely to travel long distances relative to the coarser ones which were lost during transport.
245 Likewise, in London they were associated mainly with air masses arriving from the European
246 continent.

247

248 3.2 Fe-containing Particles from Mineral Dust (Fe-DUST)

249 A significant Fe contributor to global tropospheric particulate matter is suspension of soil dusts or
250 other crustal material. The typical ATOFMS mass spectra of a dust particle type rich in Fe is shown
251 in Fig. 1b. Peaks associated with sodium (m/z 23), magnesium (m/z 24) and potassium (m/z 39) can
252 be seen. In addition, peaks for calcium (m/z 40) and aluminium (m/z 27) are present. The negative
253 spectra also show a dominant set of peaks occurring at $m/z = -16, -17, -63$ and -79 . These indicate
254 the presence of O^- , OH^- , PO_2^- and PO_3^- , respectively. Peaks of silicate (SiO_2^- and SiO_3^-) at m/z 60
255 and 76 (respectively) are also detected. This particle type was found to be the second most abundant
256 (8-11% of the total Fe-containing particles). It presented a size mode in the largest ATOFMS size
257 range at about 1.4 μm , and these were found to be the most coarse particles detected in both cities.
258 A number of studies have focused on the long-range transport of Saharan air masses over Western
259 and Eastern North Atlantic areas⁵² and across the Mediterranean.⁵³ For example, titanium rich
260 particles (along with aluminosilicate) originated from the Azores high pressure region which draws
261 air from North Africa were already identified by the ATOFMS.⁵⁴ However, during this analysis we

262 were not able to separate a specific mineral dust attributable to Saharan mineral dust, leaving this
263 ATOFMS particle type classified as general mineral dust.

264

265 3.3 Fe-containing Particles from Brake Wear (Fe-Brake)

266 Fig. 1c shows the typical mass spectra of single particles associated with brake wear material
267 originating from non exhaust traffic brake wear material.⁵⁵ Many brake linings contain high metal
268 concentrations, although there is also a large variation between different types and different brands.
269 However, the list of ingredients contained in European brake pads, notably include metallic copper,
270 steel and iron oxide, and barites, which is highly consistent with the observed correlation between
271 Cu, Ba, and Fe.¹² The characteristic features of brake wear particle types include intense $[\text{Fe}]^+$ and
272 $[\text{FeO}_2]^-$ (m/z 56 and -88) signals, along with $[\text{Ba}]^+$ and $[\text{BaO}]^+$ (m/z 138 and 154). Moreover, it was
273 noted that FeO_2^- (m/z -88) is a good indicator of brake dust particles.⁵⁵ Peaks due to copper ($[\text{Cu}]^+$,
274 m/z 63 and 65) were seen in about 30% of the particles analysed. This particle type was mainly
275 found in the supermicron mode ($>1 \mu\text{m}$). Additionally, it was found to be a major contributor near
276 the major road in London (17%) but not in Barcelona (1%, Table 1). This is likely due to the much
277 higher number of cars passing at the London site ($80,000 \text{ day}^{-1}$) than the Barcelona site ($17,000 \text{ day}^{-1}$).
278

279

280 3.4 Fe-Containing Particles from Oil Combustion (Fe-V)

281 Field observations have confirmed that ships produce significant amounts of soot, vanadium, nickel,
282 and sulfate.⁵⁶ ATOFMS studies often report a very specific particle type containing vanadium (m/z
283 51 $[\text{V}]^+$ and m/z 67 $[\text{VO}]^+$)⁵⁷⁻⁵⁸, as shown in the Art-2a cluster detected in this study (Fig. 1d). This
284 particle type was found mainly internally mixed with nitrate (m/z -46, m/z -62) and in minor
285 amount with sulphate (HSO_4^- , m/z -97). This class accounted for only 1-6% of the particles
286 characterised, with a fine aerosol unimodal distribution peaking at about 500 nm. V-containing
287 particles have been primarily attributed to residual fuel oil combustion, associated with sources such

288 as ships and refineries in the USA.⁵⁷ Likewise, the recent study of Zhang et al.³⁷ also reported this
289 particle type in Shanghai, which is a coastal mega-city with relatively high density of shipping.
290 Using single - particle online chemical analysis data, Ault et al.⁵⁷⁻⁵⁸ showed that V-containing
291 aerosols emitted from ships could contribute a large fraction of atmospheric aerosols in the
292 California basin.

293

294 **3.5. Fe-containing Particles from Combustion Mixed with Sulphate (Fe-SUL)**

295

296 The mass spectrum of this particle type (Fig. 1e) shows the presence of iron (m/z 56) and potassium
297 (m/z 39). The unique feature in the positive mass spectra is the strong peaks at m/z 27 [C₂H₃]⁺ and
298 m/z 43 [(CH₃)CO]⁺ usually associated with oxidized secondary organic aerosol.⁵⁹ Additionally, the
299 signal of sulphate (m/z -97) is the strongest of all the ATOFMS particle types described in this
300 study, hence the name characterising this particle type. This particle type contributed only 4-13% of
301 the total Fe-containing particles analysed. A key feature of particle type Fe-SUL is that it is
302 distributed in the smallest size range of the Fe-containing particles. As seen in Fig. 2, a strong mode
303 at about 350 nm can be seen, representing more than 80% of the total Fe-containing particles of this
304 size detected in this study. Overall, the finest size mode and the sulphate mixing state suggests this
305 is a combustion type particle. This particle type was similar to the ones detected in Asia^{36,37} and
306 associated with fly ash, coal and biomass burning. The frequent association of Asian dust single
307 particle mass spectra with peaks due to lithium (m/z 7, Li⁺) and to potassium (m/z 39: K⁺) was
308 indicative of a large contribution from coal combustion since biomass burning aerosols produce
309 negligible Li ion peak^{36,60}. In contrast, the absence of signal from Li in single particle mass spectra
310 reported in Fig. 1e suggests that the Fe-SUL particle type is more related to biomass burning than
311 coal combustion.

312

313 **3.6 Fe-containing Particles from Leaves/Vegetative Debris (Fe-VEG)**

314 The ATOFMS has already proved to be a good tool able to separate dust (mainly Ca-rich or Al-Si
315 rich) from biological particles⁶¹. The Art-2a cluster of Fe-VEG is shown in Fig. 1f. In addition to
316 Fe, a very strong potassium signal (K^+ at m/z 39 and 41) is attributed to biogenic sources.⁶²
317 Additionally, the biogenic plant debris origin is also supported by the presence of phosphate (m/z -
318 63, -79), as suggested in previous studies.⁵¹ This cluster was found in minor abundance (1-3%,
319 Table 1), and presented a broad size distribution (Fig. 2, 51% super- μm , 49% sub- μm). K-rich
320 particles have previously been attributed to biomass burning^{60,63} and have been found to correlate
321 with gas-phase measurements of acetonitrile, a good biomass-burning tracer. However, the presence
322 of peaks at m/z 39 [K^+], m/z 113 [K_2Cl^+] and m/z -35 [Cl^-] suggesting a combustion source related
323 to biomass burning are not seen in the particle mass spectra, excluding such a source.

324

325 4. DISCUSSION

326

327 This work aims to better understand the aerosol sources of fine Fe-containing particles and their
328 aerosol mixing state in the European atmosphere. Single particle mass spectrometry (ATOFMS)
329 was used to acquire more than 1,500,000 positive and negative mass spectra of single particle of
330 known size. It is important to stress the fact that whilst the ATOFMS provides important
331 information on the mixing state of the aerosols and temporal trends of unique particle types over
332 time, the total number of particles sampled by the instrument does not have quantitative meaning
333 without extensive calibrations as it is biased by transmission efficiency⁶⁴. Nevertheless, the
334 ATOFMS can precisely size particles within the 0.3-1.5 μm range. The six particle types identified
335 were mostly distributed in the submicron mode ($<1 \mu\text{m}$): Fe-LRT (72% of the particles were
336 smaller than 1 μm), Fe-SUL (99%) and Fe-V (76%). Vegetative dust (Fe-P) was equally distributed
337 (51% submicron, 49% supermicron). By contrast, mineral dust and brake dust were found more
338 abundant in the supermicron ($>1 \mu\text{m}$) size range: 82% and 73%, respectively, as found in previous
339 studies^{5,6}.

340 This study - unique in the aspect that it analyses submicron Fe-containing particles at very high time
341 resolution at two European sites - suggests that the main contribution of submicron iron particles by
342 particle number is related to regional and long range transport of aerosol. The most abundant Fe-
343 containing particle type (54-82%) was found to be associated with nitrate, and the absence of
344 mineral dust peaks (Al, Ti, Ca, Si) suggests an anthropogenic urban-industrial source. Fe-containing
345 particles from long range transport have a size distribution peaking at about 600 nm. Previous
346 studies in the same location in London support our findings. Charron et al.⁶⁵ found that the regional
347 background aerosol was the largest contributor measured at Marylebone Road between January
348 2002 and December 2004. Very often these episodes were associated with air masses coming from
349 mainland Europe which carried large concentrations of secondary aerosol adding particulate mass to
350 primary emissions from local urban sources around London.

351

352 By contrast, local sources were found to contribute only in small percentages to Fe aerosol particle
353 concentrations. In urban areas, local road traffic is recognised as an important source of particulate
354 matter (PM). Numerous studies have been conducted regarding traffic-emitted pollutants, with most
355 investigations focusing on exhaust emissions. The most important direct emission sources are the
356 wear of tyres, brakes, and road surfaces. None of the six Fe-containing particle types detected at the
357 two road sites used in this study correlated temporally with the traffic counts. Meteorological data
358 was examined for correlation with aerosol types. However, only a weak correlation between brake
359 wear (Fe-Brake) and wind speed ($R^2 = 0.25$ and 0.41 at LND and BCN, respectively) was observed.
360 As expected, mineral dust was found to be a major source of Fe-particles in both Barcelona and
361 London. However, an interesting finding of this work is that at the heavily trafficked London road
362 site, brake wear was found to contribute a higher percentage by number (17%) than mineral dust
363 (8%). Another minor anthropogenic source containing iron was associated with the marine
364 transport sector (ATOFMS Fe-V), which is especially polluting due to the use of low-quality
365 residual fuels containing high amounts of sulphur and heavy metals. Concentrations of V are

366 elevated in the Mediterranean region owing to increased consumption of fuel oil for power
367 generation, shipping and industrial emissions^{66,67}. In this study the ATOFMS Fe-V particle type
368 was found to be highly correlated with Fe-LRT (temporal $R^2 = 0.85$), suggesting that this particle
369 type is also primarily related to long range transport rather than to local shipping from the nearby
370 ports of Barcelona and London. With regards to other combustion sources, it is important to
371 recognise that particles associated with biomass burning/coal combustion contribute only 4-13% of
372 the particles sampled at the two European sites. This is in profound contrast to studies of the same
373 type conducted in Asia, where comparing the chemical composition and spatial distribution of iron
374 within ambient particles and standard Asian mineral dust, it was determined that the main source of
375 field collected atmospheric Fe-containing particles was coal combustion.^{36,37}

376

377 One limitation of this study is that the ATOFMS uses a laser desorption/ionization (LDI). Such
378 process is heavily influenced by particle size, morphology and matrix composition, since these will
379 influence energy transfer from the laser beam to the particle, vaporization of the particle and ion
380 formation in the vaporization plume. As a result, whilst the ATOFMS can provide the precise
381 aerodynamic diameter of individual particles, the chemical information obtained by this type of
382 single particle mass spectrometry can only be treated as qualitative, or semi-quantitative after a
383 complex calibration⁶⁸. Luckily, there are a number of filter-based off line studies that have focused
384 on the aerosol mass source apportionment of Fe in the PM_{10} and $PM_{2.5}$ aerosol size fraction.
385 Interestingly, in the coarse fraction ($PM > 2.5 \mu m$) Fe is usually associated with mineral dust, road
386 dust and traffic related matter. However, the source distribution of Fe in the finer size fraction is not
387 clear at all. In the city of Barcelona, Amato et al.⁶⁷ reported that major sources of $PM_{2.5}$ Fe are due
388 to mineral and industrial activity. However, about 15-30% of the PM_{10} and $PM_{2.5}$ Fe was attributed
389 to secondary more aged material not of local origin. Cusack et al.⁸ reported a detailed source
390 apportionment of PM_{10} at a regional background site in the western Mediterranean. It was found that
391 about 45% of PM_{10} iron was associated with secondary sulphate and secondary organic aerosol.

392 Perrone et al.⁹ reported almost two years of data of PM_{2.5} and PM₁ samples collected at a central
393 Mediterranean site. It was found that 60% of the aerosol mass PM_{2.5} occurred in the PM₁ range .
394 The PM source identification showed that Fe in the PM_{2.5} was distributed almost equally between
395 four sources: reacted dust, heavy oil combustion, secondary marine and traffic. Within the PM₁
396 mass region, Perrone et al.⁹ reported that about 60% of the Fe was related to long range transport
397 sources: nitrate with reacted dust, secondary marine and ammonium sulphate. During the same
398 SAPUSS field campaign used in this work, Dall'Osto⁷ reported hourly metal concentrations. PM_{2.5}
399 Fe was higher at the road site than the urban background site, stressing the importance of traffic
400 activities. About 70% was related to non-exhaust traffic activity, and the rest to industry (about
401 10%) and dust (about 20%). However, nitrate was not detectable by the analytical technique used
402 (PIXE), so the results from this study cannot readily be compared. Fewer studies are available in
403 London, although recently Visser et al.¹⁰ reported a very detailed study of the kerb and urban
404 increment of highly time-resolved trace elements in PM₁₀, PM_{2.5} and PM₁ aerosol in London. While
405 the PM_{2.5-10}/PM_{0.3-1} Fe aerosol mass ratio at the road site was found to be 7.7, it was less at the
406 background sites (5.5 and 5.6), suggesting the higher importance of fine Fe-containing aerosols
407 away from traffic sources. Indeed - regardless of the local impact of vehicles at each monitoring site
408 - this study shows that most of the fine Fe-containing particles detected are related to long range
409 transport.

410

411 Another interesting finding is that the major particle type characterised in this study - related to
412 regional and long range transport - is internally mixed with nitrate. Our results are in profound
413 contrast with previous important work carried out in Asia, where Fe-containing particles were found
414 to be internally mixed with secondary species such as sulphate, soot, and organic carbon, but not
415 nitrate.^{21,36,37} . It is relevant that within the European Union (EU), in the last decades much lower
416 SO₂ levels are being recorded following strict implementation of industrial pollution controls⁶⁹. EU
417 abatement of traffic related NO_x levels is still required to maintain levels within international

418 standards⁶⁹. Control actions in Asia have also been taken, although their effectiveness is outweighed
419 by increased energy demand, with larger amount of SO₂ from coal relative to Europe⁷⁰⁻⁷¹. The fact
420 that our detected long range transport Fe-containing aerosols are internally mixed with nitrate is not
421 surprising given the higher amount of NO_x relative to SO₂ in the urban atmosphere, whereas the
422 latter has much higher concentrations in Asia. As regards of the seasonality of the studied main Fe
423 particle type (Fe-LRT), the two field studies herein reported were carried out in spring (London)
424 and fall (Barcelona). Whilst previous analysis show a reduction due to evaporation of nitrate during
425 warm summer months, the evolution of nitrate can be heavily influenced by meteorological
426 factors⁷². Given the likely urban anthropogenic source of fine iron-nitrate particles, we speculate the
427 mixing state may not change dramatically across most of the year.

428 We looked at iron containing particles sampled by ATOFMS at other European sites. A previous
429 study of the size distributions and the chemical characterization of airborne particles in the vicinity
430 of a large integrated European steelworks⁷³ found that Fe-rich particles were mainly related to
431 emissions from the blast furnace as a result of furnace tapping and slag quenching operations. It was
432 found that Fe-rich particles are internally mixed with nitrate (and very little sulphate), reporting
433 mass spectra similar to those shown in Figure 1a, suggesting a contribution of this source to the
434 ATOFMS Fe-LRT particle type. Data sets from two other studies carried out at Mace Head,
435 Ireland²⁶ and in the Po Valley, Italy⁷⁴ were queried for fine Fe-containing particles. It was found
436 that most of the fine Fe containing particles are of anthropogenic origin and internally mixed with
437 nitrate - consistent with this study. However, Fe-containing particles represented less than 0.5% of
438 the total sampled particles.

439

440 We did not study the solubility of the detected particles. Generally, Fe-nitrate chemical species are
441 usually more soluble than Fe-sulphate species. Baker and Jickells¹⁸ reported an inverse relationship
442 between dust mass concentration and FFS, arguing that the greater solubility at lower dust mass
443 concentration could be due to a larger surface area to volume ratio of the finer dust particles.

444 However, later studies¹⁷⁻¹⁹ reported that the size dependence of the FFS can at most explain a small
445 part of the measured variability in FFS in atmospheric aerosol samples. Overall, natural Fe-dust is
446 generally found in the coarser mode than anthropogenic urban related Fe-dust²². While no
447 conclusions can be drawn on aerosol solubility, this study shows that the main type of fine Fe-
448 containing particles in the urban atmosphere are internally mixed with nitrate, hence of different
449 chemical composition of natural Fe-dust. Additionally, it is important to remember that while
450 sulphate is not considered a nutrient for marine microorganisms, nitrate is a key one, alongside iron.
451 Atmospheric reactive nitrogen is mainly derived from anthropogenic combustion or agricultural
452 sources in densely populated regions throughout the world.³⁰ The supply of new nutrients to the
453 ocean from external sources such as atmospheric deposition has been extensively addressed in iron-
454 limited High Nutrient-Low Chlorophyll (HNLC) regions,³¹ most of which receive low atmospheric
455 inputs at the present time.³² How the ocean responds to pulses of deposition - as either transient or
456 long-term impacts on diversity of the natural assemblage and/or carbon export - is not obvious.
457 Guieu et al.⁵⁸ recently reviewed the significance of the episodic nature of atmospheric deposition to
458 low nutrient LNLC regions. Most of the experimental studies presented used desert dust but few
459 considered its solubility and hence bioavailability. This is particularly important because desert
460 dusts derived from soils contain very little soluble nitrogen whereas “atmospherically processed
461 dust” is rich in nitrogen. It was stressed that differences in the source of the material used (e.g., soil
462 vs. locally collected aerosols), related composition, and solubility may partially explain the
463 observed variability in response. Deposition of iron, nitrogen, phosphorus and organic matter has
464 increased considerably since preindustrial times³⁰ and nitrogen could further slightly increase in the
465 future (Guieu et al.³² and ref. included). The present study shows that anthropogenic Fe-containing
466 particles also contain nitrate, and the interactive effects and the possible synergy of both nutrients is
467 not currently accounted for in ocean global biogeochemical cycles. The solubility of Fe in
468 atmospheric aerosols, model soils, and desert samples has been investigated thoroughly in various
469 ocean and atmospheric environments during the past decade,¹⁷⁻¹⁹ illustrating the complex nature of

470 iron solubility in atmospheric aerosols. This study shows that the majority of fine Fe-containing
471 particles collected in urban European environment are internally mixed with nitrate, and it is
472 important to keep this in mind when studying both the health effects of urban aerosol and the
473 impact of iron in LNLC-HNLC oceanic regions impacted by long range transport of European
474 anthropogenic aerosol.

475

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789 **TABLE LEGEND**

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791 **Table 1:** Major types of Fe-containing particles identified by the ATOFMS, and their
792 abundance in the Barcelona (BCN) and London (LND) studies.

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795 **FIGURE LEGENDS**

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797 **Figure 1:** Positive and Negative ART-2a area vectors attributed to (a) Fe-LRT, (b) Fe-Dust,
798 (c) Fe-Brake, (d) Fe-V, (e) Fe-SUL and (f) Fe-P.

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801 **Figure 2:** Size distributions of the six different particle types detected at the two European
802 sites. It is clear that combustion Fe-SUL are in the fine mode, the nitrate-Fe in the
803 accumulation mode, and the Fe-Brake and Fe-Dust in the coarser mode. Fe-V in the
804 fine combustion mode, Fe-P (vegetative debris) is bimodal in both fine and coarse
805 modes.

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820 Table 1: Major types of Fe-containing particles identified by the ATOFMS, and their abundance in
821 the Barcelona (BCN) and London (LND) studies. In the text the interval of the % are given as %
822 across the two monitoring sites (BCN and LND, i.e. Fe_LRT is 54-82%).
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ATOFMS particle type	Total particle number		%	
	BCN	LND	BCN	LND
Fe_LRT	5221	2254	82	54
Fe_Dust	664	344	11	8
Fe_Brake	41	695	1	17
Fe_V	61	244	1	6
Fe_SUL	282	524	4	13
Fe_P	106	113	1	3
Total	6375	4174	100	100

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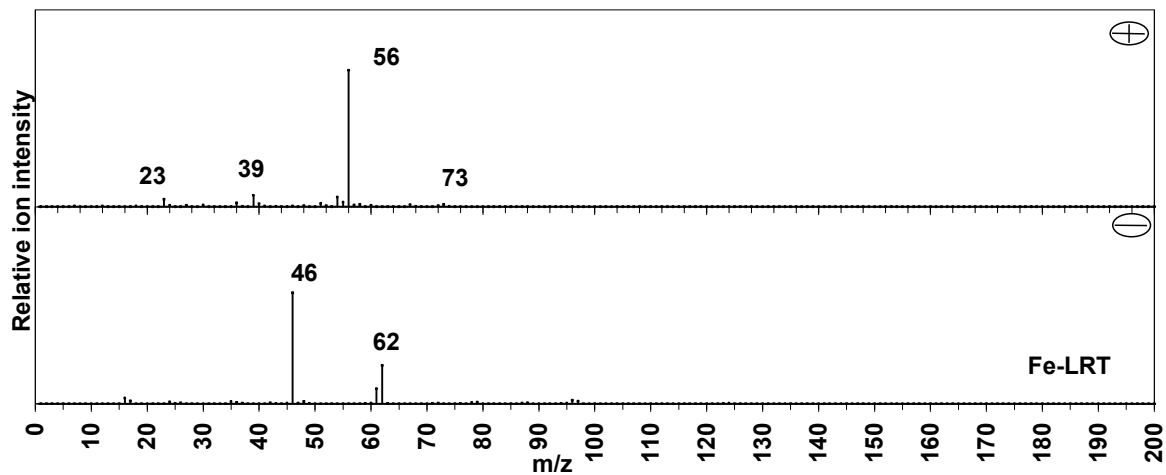
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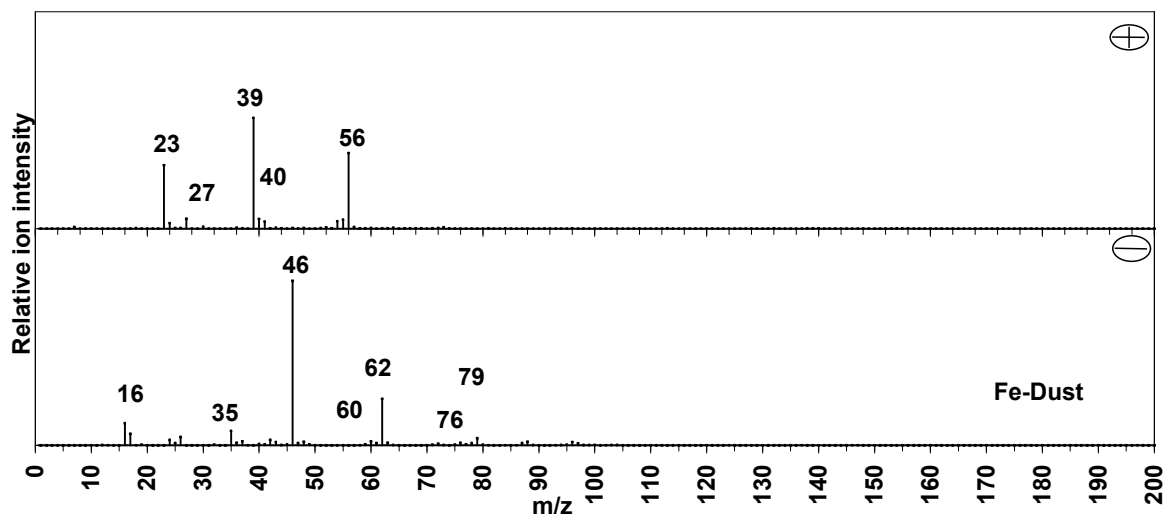


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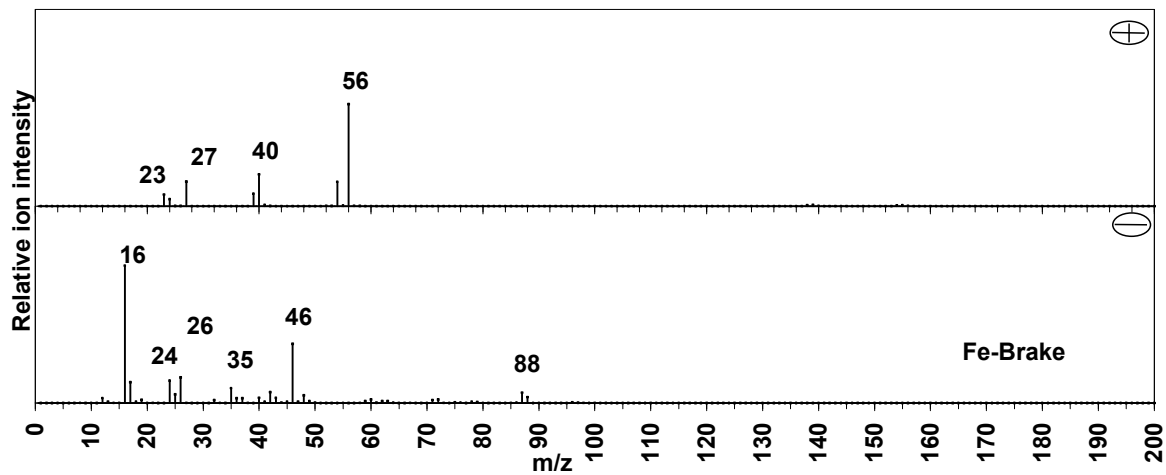
(a)



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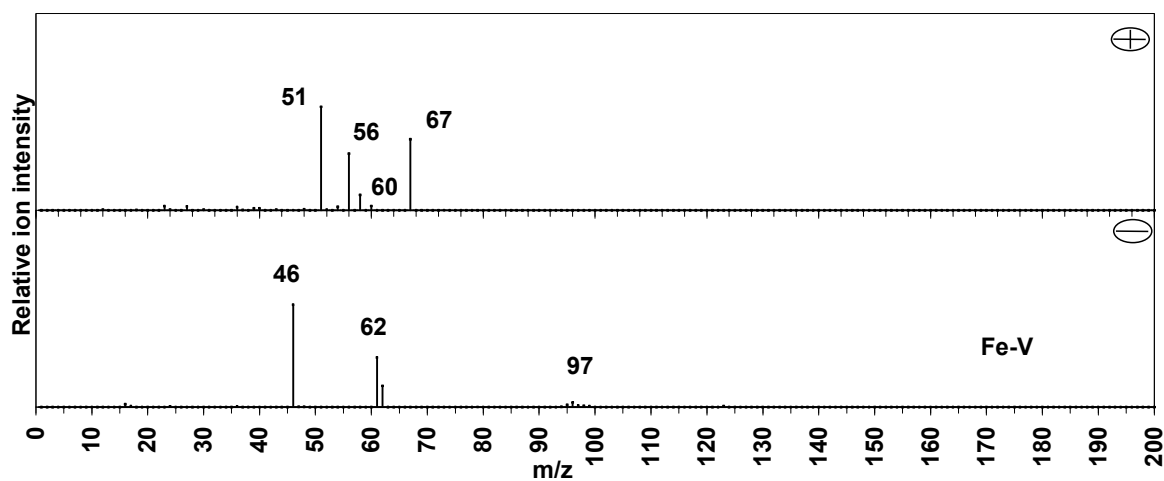


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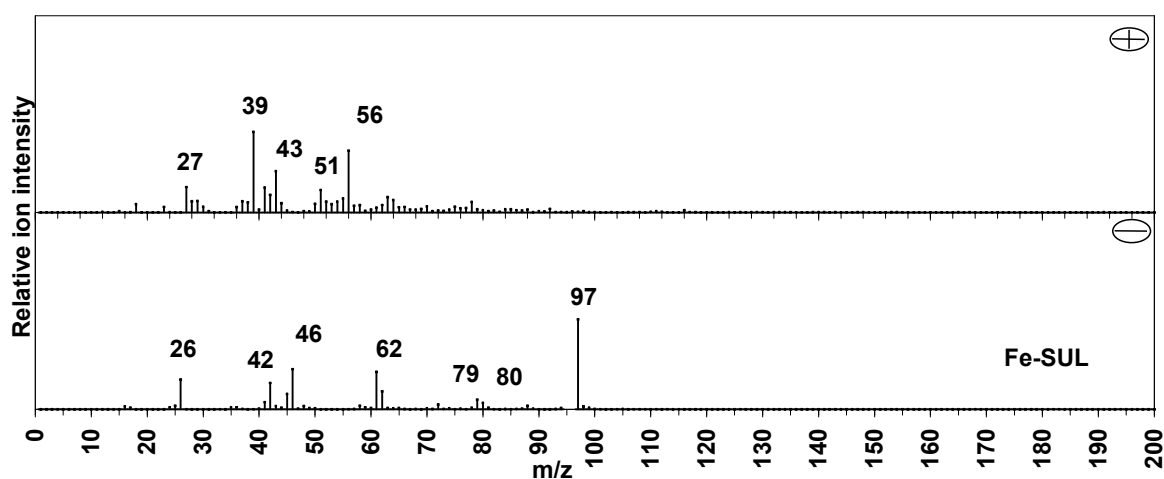
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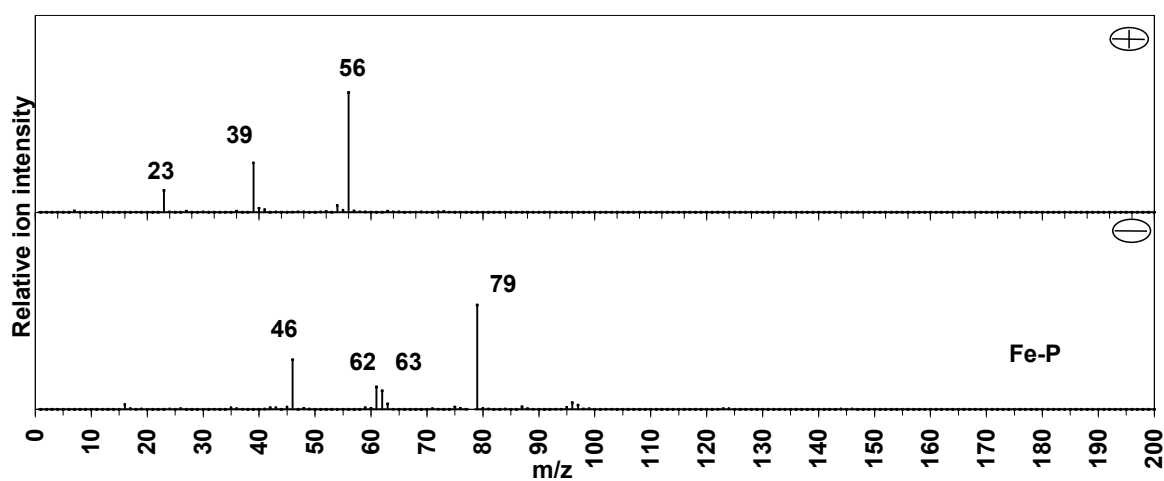
(c)

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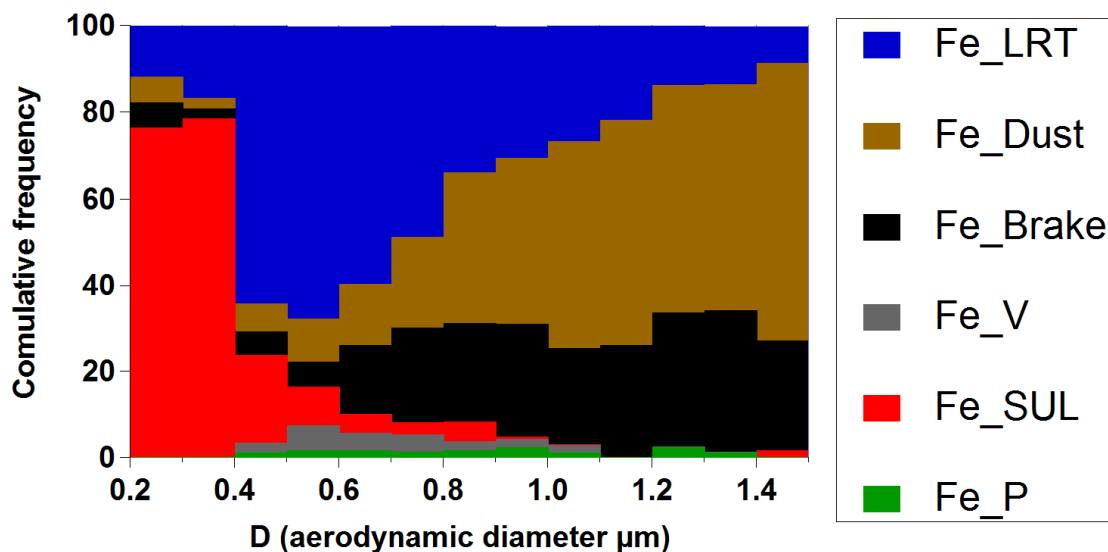
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850 Figure 1: Positive and Negative ART-2a area vectors attributed to (a) Fe-LRT, (b) Fe-Dust, (c) Fe-
851 Brake, (d) Fe-V, (e) Fe-SUL and (f) Fe-P. Peaks above m/z 200 were minor and are not reported.

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Figure 2: Size distributions of the six different particle types detected at the two European sites. It is clear that combustion Fe-SUL are in the fine mode, the nitrate-Fe in the accumulation mode, and the Fe-Brake and Fe-Dust in the coarser mode. Fe-V in the fine combustion mode, Fe-P (vegetative debris) is bimodal in both fine and coarse modes.