University of Birmingham
Research at Birmingham

Fine iron aerosols are internally mixed with nitrate in the urban european atmosphere

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

DOI:
10.1021/acs.est.6b01127

License:
None: All rights reserved

Document Version
Peer reviewed version

Citation for published version (Harvard):
Dall'Osto, M, Beddows, D, Harrison, R & Onat, B 2016, 'Fine iron aerosols are internally mixed with nitrate in the urban european atmosphere', *Environmental Science and Technology*, vol. 50, no. 8, pp. 4212-4220. https://doi.org/10.1021/acs.est.6b01127

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
Checked for eligibility: 08/04/2016

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

•Users may freely distribute the URL that is used to identify this publication.
•Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
•User may use extracts from the document in line with the concept of ‘fair dealing’ under the Copyright, Designs and Patents Act 1988 (?)
•Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 19. Apr. 2024

Environmental Science & Technology

UNIVERSITY OF BIRMINGHAM

Subscriber access provided by University of Birmingham

Article

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

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

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.6b01127 • Publication Date (Web): 22 Mar 2016

Downloaded from http://pubs.acs.org on March 31, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications

Environmental Science & Technology is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

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

M. Dall´Osto[1*], D.C.S. Beddows[2], Roy M. Harrison[2†] and Burcu Onat [3]

[1]Departament de Biologia Marina i Oceanografia
Institut de Ciències del Mar, CSIC
Pg. Marítim de la Barceloneta, 37-49
08003 Barcelona, Catalonia, Spain

[2]Division of Environmental Health and Risk Management
School of Geography, Earth and Environmental Sciences
University of Birmingham, Edgbaston, Birmingham, B15 2TT
United Kingdom

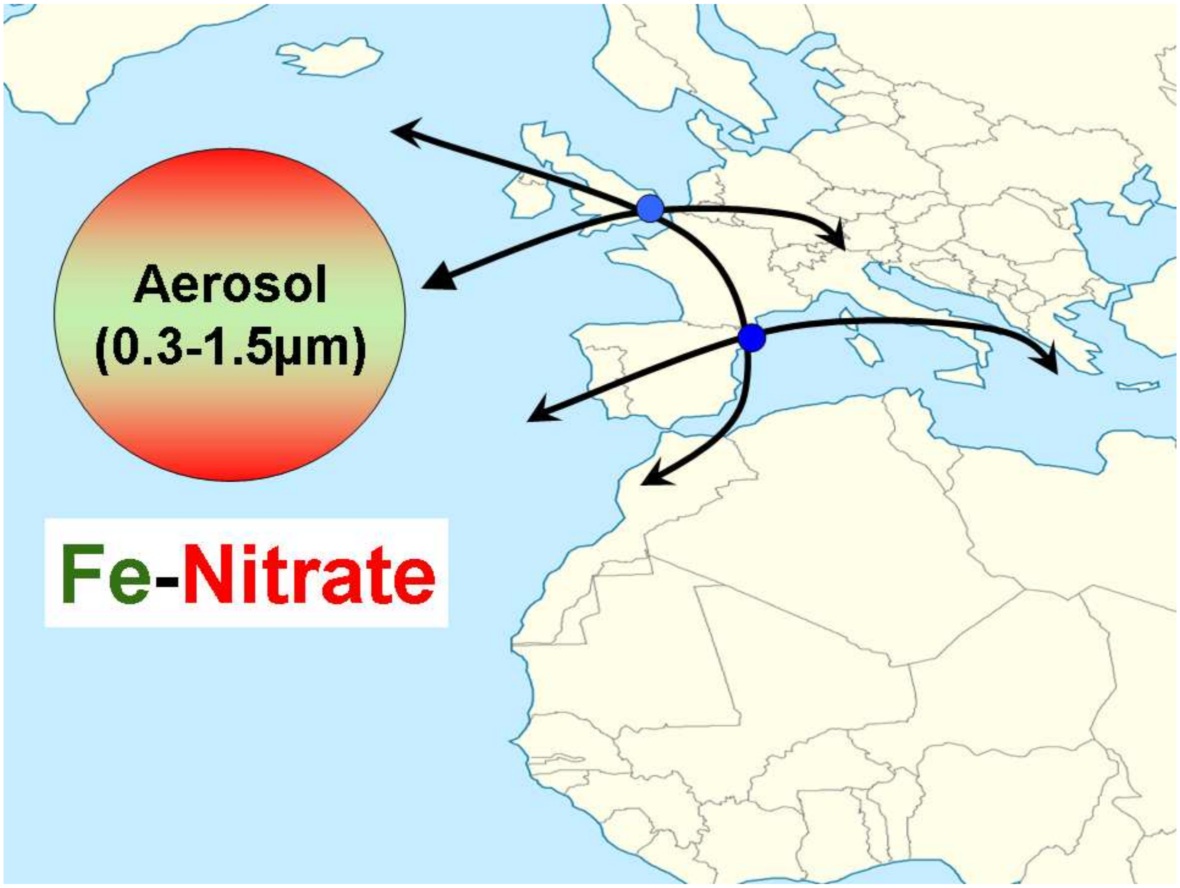
[3]Istanbul University
Environmental Engineering Department
Avcilar 34320, Istanbul, Turkey

---

[*] 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

TOC



ABSTRACT

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

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

1. INTRODUCTION

Atmospheric particulate matter (PM) has well known adverse effects on human health[1] and atmospheric visibility; and partly compensates climate forcing by greenhouse gases.[2] Iron (Fe) is a major element found in the atmospheric aerosol. Atmospheric Fe has both natural (e.g. aeolian desert dust transport) and anthropogenic (e.g. iron/steel and general industrial activities, traffic) origins.[3,4] Coarse particles ($PM_{2.5\text{-}10}$) are often considered to be related to crustal elements and resuspension of road dust.[4] However - within the urban environment - Harrison et al.[5] found that the iron concentration within coarse dusts was much greater at roadside sites than at urban background sites and this was considered indicative of road traffic and most probably the vehicles themselves as a source. Gietl et al.[6] also showed that Fe and other brake wear elements (Cu, Ba, Sb) have very similar particle size distributions at a roadside site, implying a common source. Dall´Osto et al.[7] found that Fe and Cu together can also be used as a tracer of brake wear also in $PM_{2.5}$ aerosol sampled in the urban agglomerate of Barcelona (Spain).

In general little is known about aerosol sources of Fe-containing particles in the finer mode (PM_1)[8-9-10] in the urban atmosphere. Although fine aerosol modes contribute little Fe to the total aerosol mass, it has much greater potential for respiratory intake, and its involvement in health effects. Fe is a transition metal which is considered to exert toxic effects, which may release free radicals in lung tissues via the Fenton reaction, and are hypothesized to cause cellular inflammation.[11,12] Iron aerosol particle size influences their reactivity, toxicity and solubility.[13] Since particle-bound metals need to dissolve and become free ions in the lung fluid, particle solubility is considered a major criterion for the bioavailability and therefore toxicity.[12,14] Atmospheric Fe may be associated with adverse health effects due to mechanisms such as DNA strand breakage and tissue or cell damage.[15]

Fine Fe plays a role also in ocean/climate biogeochemical cycles, and it might actually be more important than coarse Fe-containing aerosol[16,17]. Briefly, iron is an essential nutrient for all organisms, used in a variety of enzyme systems, including those for photosynthesis, respiration, and nitrogen fixation.[16] Several studies have argued that the greater solubility at lower dust mass concentration could be due to a larger surface area to volume ratio of the finer dust particles.[17-19] However, the size dependence of the fractional Fe solubility (FFS) can at most explain a small part of the measured variability in FFS in atmospheric aerosol samples. The high values of the FFS of > 1% in atmospheric aerosol samples are related to a number of atmospheric processes and natural and anthropogenic sources and are clearly not well understood.[17] It is also important to keep in mind that although combustion sources are not important for the total Fe mass compared to natural sources, they can contribute up to 50% of soluble Fe deposited into oceanic regions[20-21]. Overall, the relationships between iron solubility, oxidation state, and bioavailability are complex and poorly understood.

Evidence for the importance of such a dust–ocean–climate feedback process is still limited. Whilst the role of desert dust is currently being studied[17-20], far less information is available on Fe-containing urban anthropogenic dust[22] . Urban influenced air masses can travel long distances. Continental polar air masses originating in Europe travel southwards across the Mediterranean, North Africa and finally reach the tropical Atlantic Ocean[23]. Continental polar air masses originating in Portugal and Ireland also travel southwards to the Canary Island waters[24]. Northern European air masses originating in the continent of Europe can travel across the British Isles and further to the North Atlantic Ocean. For example, results from Mace Head (Ireland) show that these continental polar air masses travel to the Atlantic Ocean fairly often, about a third of the time[25-26]. Once urban anthropogenic dust is deposited in the ocean, its impact on marine productivity will depend on a number of factors, including the bioavailability of the chemical components present in the dust[3,27,28].

In order to characterise the sources, transport and transformations of Fe aerosols in the atmosphere, a comprehensive approach that simultaneously characterises single particles for aerodynamic diameter and chemical composition is needed[29]. The use of single-particle analysis is an important analytical tool because it allows determination of how the chemical constituents are distributed between individual particles (mixing state). Specifically, in this work we are interested in apportioning which secondary chemical components (i.e. nitrate, sulphate) are mixed within Fe containing aerosols; because this can have implications for solubility and additional nutrient capability[30-32]. We use Aerosol Time-of-Flight Mass Spectrometry (ATOFMS), which provides information on the abundance of different types of aerosol particles as a function of particle size with a much high time resolution and better count statistics[29]. For the purpose of our work, the ATOFMS is more suitable than other single particle techniques. For example, Transmission electron microscopy (TEM) is a powerful technique capable of simultaneously obtaining unique information on individual particles regarding metal speciation, size, mixing state, and morphology[33-34]. However, semi-volatile particle types (i.e. nitrate) are liable to vaporise in the high vacuum environment of the TEM and therefore not be observed[35].

A few specific studies reporting the sources and mixing state of iron-containing particles can be found in the literature. Furutani et al.[36] utilized single particle mass spectrometry to classify Fe-containing particles based on their chemical associations. Fe-containing particles have numerous sources, especially anthropogenic sources such as coal combustion. Indeed, mineral dust was found to be a minor contributor to the total iron concentration, whereas the importance of the coal combustion source in East Asia was emphasised. Complementary measurements[21,36] performed at the same time and location[18] showed that field-collected atmospheric Fe-containing particles were found to be internally mixed with secondary species such as sulfate, soot, and organic carbon. Recently, Zhang et al.[37] showed ATOFMS results collected in Shanghai (China) for nearly 22 d during the winter of 2011. Fe-containing particles were mainly clustered into four chemical groups, comprising Fe-rich, K-rich, Dust and V-containing particle types. It was concluded that major sources of Fe-containing particles correspond to various anthropogenic sources including iron/steel industrial activities, and fly ash from both biomass burning and coal combustion, accounting for 55% and 18%, respectively. Hu et al.[38] also stressed that sources of Fe-bearing particles in the Beijing atmosphere (China) are mainly local steel industries and oil fuel combustion. As a consquence, the majority of the Fe-containing particles collected in Asia are found to be mainly internally mixed with sulphate [21,36-38]. With regard to other study areas, to our knowledge there are not specific ATOFMS studies on the matter.

In summary, whilst coarse Fe-containing particles ($PM_{2.5-10}$) are often associated with mineral dust, road dust and non-exhaust traffic material, little is known of the sources of finer Fe-containing particles. Furthermore, to our knowledge all aerosol mixing state studies on Fe-containing particle studies presented in the literature discuss ambient data collected in Asia. This study reports information on sources and mixing state of Fe-containing particles sampled over the European continent. Both meteorology and emissions show large variations across Europe, and conclusions from a certain region cannot necessarily be extrapolated to other parts of the continent. Latitude variations within Europe influence mineral matter[39], Saharan dust intrusion[40], secondary inorganic aerosol[41] and sea salt concentrations[42].For this reason, we consider two different ambient ATOFMS datasets from Barcelona (Spain) and London (England). Whilst both monitoring sites are classified as "roadside" sites, the Spanish one presents a minor road in an environment subject to more Saharan dust intrusion in a drier climate.[26] By contrast, the monitoring site in London is near a major road under typical North European weather conditions.[44] We use two road side sites cause we want to apportion both local road traffic[22] and regional long range transport sources. Further ATOFMS studies previously published in other background European locations (Mace Head, Ireland; Po Valley, Italy and Port Talbot, Wales) are also compared with the presented results. Different aerosol sources are inferred and discussed, including their average aerosol sizes and mixing state. An important comparison with existing ATOFMS data collected in Asia is also presented, and its implication for marine biogeochemistry discussed.

2. METHODS

2.1 Locations

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

With regard to air mass back trajectory analysis run for the two ambient field campaigns herein presented, it was shown in previous studies that air masses travelling over the study areas continue to travel and reach nearby and far oceans and seas about a quarter of the ambient field study time[43,46]

2.2 Instrumentation

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

Depending on the scientific objectives, past studies have typically used the aerodynamic lens system to study ultrafine and fine anthropogenic emissions[49] or the nozzle orifice system to study dust particles.[21] In this study we focus on fine aerosol, so we chose the aerodynamic lens system configuration for better count statistics. Additionally, it is important to note that this study uses the same ATOFMS aerodynamic lens configuration used in past ATOFMS studies characterising Fe-containing particles in Asia.[21,36,37]

Fe-containing particles commonly produce an intense ion peak at mass-to-charge ratio (m/z) 56 in the positive ion mass spectrum. As discussed in Zhang et al.[37], simply using the ion peak at m/z 56 as a unique marker for Fe is not suitable, since it might also be caused by the presence of CaO^+, KOH^+, or $C_3H_4O^+$ from other components. There are also other contributors (mainly organic) at m/z = 54. Therefore, as previously described[36,37] the natural isotopic composition of Fe ($^{54}Fe/^{56}Fe$) was adopted as a basis for the Fe screening process to minimize the interference from other species. A peak-area ratio $^{56}Fe/^{54}Fe > 10$ was finally applied as recommended by Zhang et al.[37] to strengthen the screening through excluding more ambiguous assignments. The screened Fe-containing particles were subsequently imported into YAADA (Yet Another ATOFMS Data Analyzer) and single-particle mass spectra were grouped with adaptive resonance theory neural network, ART-2a.[50] The parameters used for ART-2a in this experiment were: learning rate 0.05, vigilance factor 0.85, and 20 iterations. Further details of the parameters can be found elsewhere.[37] An ART-2a area matrix (AM) of a particle cluster represents the average intensity for each m/z for all particles within a group. An ART-2a AM therefore reflects the typical mass spectra of the particles within a group.

3. RESULTS

Overall, 890,873 and 693,462 ATOFMS mass spectra were apportioned in Barcelona[43] and London[46], respectively. The two datasets were merged and the resulting total number of particles (1,584,335) were queried for Fe following the methodology explained in section 2.2, and a total number of 10,549 particles (6,375 in Barcelona, 4,174 in London) were found. By running ART-2a on the combined dataset, more than 300 clusters were found initially but many were merged if they presented similar temporal trends, size distributions and similar mass spectra.[51] By merging similar clusters, the total number of clusters describing the whole database was reduced to six, which are described in the following sub-sections.

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

This was found to be the most frequently occurring cluster (54-82%, Table 1). The average ATOFMS Art-2a cluster (Fig. 1a) shows strong signals at m/z 54 and 56 (^{54}Fe and ^{56}Fe, respectively) and iron oxide ($[FeOH]^+$, m/z 73). It is found internally mixed with nitrate (m/z -46 and -62 in the negative spectra). This particle type was mainly distributed in the fine mode peaking at around 0.4-0.7 µm in aerodynamic diameter (Fig. 2). In Barcelona, Fe-rich particles were found to correlate with ATOFMS Long Range Transport (LRT) nitrate associated with long range transport of pollutants[43]. The small mode of this particle type reflects the fact that only fine particles were likely to travel long distances relative to the coarser ones which were lost during transport. Likewise, in London they were associated mainly with air masses arriving from the European continent.

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

A significant Fe contributor to global tropospheric particulate matter is suspension of soil dusts or other crustal material. The typical ATOFMS mass spectra of a dust particle type rich in Fe is shown in Fig. 1b. Peaks associated with sodium (m/z 23), magnesium (m/z 24) and potassium (m/z 39) can be seen. In addition, peaks for calcium (m/z 40) and aluminium (m/z 27) are present. The negative spectra also show a dominant set of peaks occurring at m/z = -16, -17, -63 and -79. These indicate the presence of O^-, OH^-, PO_2^- and PO_3^-, respectively. Peaks of silicate (SiO_2^- and SiO_3^-) at m/z 60 and 76 (respectively) are also detected. This particle type was found to be the second most abundant (8-11% of the total Fe-containing particles). It presented a size mode in the largest ATOFMS size range at about 1.4 µm, and these were found to be the most coarse particles detected in both cities. A number of studies have focused on the long-range transport of Saharan air masses over Western and Eastern North Atlantic areas[52] and across the Mediterranean.[53] For example, titanium rich particles (along with aluminosilicate) originated from the Azores high pressure region which draws air from North Africa were already identified by the ATOFMS.[54] However, during this analysis we were not able to separate a specific mineral dust attributable to Saharan mineral dust, leaving this ATOFMS particle type classified as general mineral dust.

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

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

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

Field observations have confirmed that ships produce significant amounts of soot, vanadium, nickel, and sulfate.[56] ATOFMS studies often report a very specific particle type containing vanadium (m/z 51 $[V]^+$ and m/z 67 $[VO]^+$)[57-58], as shown in the Art-2a cluster detected in this study (Fig. 1d). This particle type was found mainly internally mixed with nitrate (m/z -46, m/z -62) and in minor amount with sulphate (HSO_4^-, m/z -97). This class accounted for only 1-6% of the particles characterised, with a fine aerosol unimodal distribution peaking at about 500 nm. V-containing particles have been primarily attributed to residual fuel oil combustion, associated with sources such as ships and refineries in the USA.[57] Likewise, the recent study of Zhang et al.[37] also reported this particle type in Shanghai, which is a coastal mega-city with relatively high density of shipping. Using single‐particle online chemical analysis data, Ault et al.[57-58] showed that V-containing aerosols emitted from ships could contribute a large fraction of atmospheric aerosols in the California basin.

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

The mass spectrum of this particle type (Fig. 1e) shows the presence of iron (m/z 56) and potassium (m/z 39). The unique feature in the positive mass spectra is the strong peaks at m/z 27 $[C_2H_3]^+$ and m/z 43 $[(CH_3)CO]^+$ usually associated with oxidized secondary organic aerosol.[59] Additionally, the signal of sulphate (m/z -97) is the strongest of all the ATOFMS particle types described in this study, hence the name characterising this particle type. This particle type contributed only 4-13% of the total Fe-containing particles analysed. A key feature of particle type Fe-SUL is that it is distributed in the smallest size range of the Fe-containing particles. As seen in Fig. 2, a strong mode at about 350 nm can be seen, representing more than 80% of the total Fe-containing particles of this size detected in this study. Overall, the finest size mode and the sulphate mixing state suggests this is a combustion type particle. This particle type was similar to the ones detected in Asia[36,37] and associated with fly ash, coal and biomass burning. The frequent association of Asian dust single particle mass spectra with peaks due to lithium (m/z 7, Li^+) and to potassium (m/z 39: K^+) was indicative of a large contribution from coal combustion since biomass burning aerosols produce negligible Li ion peak[36,60]. In contrast, the absence of signal from Li in single particle mass spectra reported in Fig. 1e suggests that the Fe-SUL particle type is more related to biomass burning than coal combustion.

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

The ATOFMS has already proved to be a good tool able to separate dust (mainly Ca-rich or Al-Si rich) from biological particles[61]. The Art-2a cluster of Fe-VEG is shown in Fig. 1f. In addition to Fe, a very strong potassium signal (K^+ at m/z 39 and 41) is attributed to biogenic sources.[62] Additionally, the biogenic plant debris origin is also supported by the presence of phosphate (m/z -63, -79), as suggested in previous studies.[51] This cluster was found in minor abundance (1-3%, Table 1), and presented a broad size distribution (Fig. 2, 51% super-μm, 49% sub-μm). K-rich particles have previously been attributed to biomass burning[60,63] and have been found to correlate with gas-phase measurements of acetonitrile, a good biomass-burning tracer. However, the presence of peaks at m/z 39 $[K]^+$, m/z 113 $[K_2Cl]^+$ and m/z -35 $[Cl]^-$ suggesting a combustion source related to biomass burning are not seen in the particle mass spectra, excluding such a source.

4. DISCUSSION

This work aims to better understand the aerosol sources of fine Fe-containing particles and their aerosol mixing state in the European atmosphere. Single particle mass spectrometry (ATOFMS) was used to acquire more than 1,500,000 positive and negative mass spectra of single particle of known size. It is important to stress the fact that whilst the ATOFMS provides important information on the mixing state of the aerosols and temporal trends of unique particle types over time, the total number of particles sampled by the instrument does not have quantitative meaning without extensive calibrations as it is biased by transmission efficiency[64]. Nevertheless, the ATOFMS can precisely size particles within the 0.3-1.5 μm range. The six particle types identified were mostly distributed in the submicron mode (<1 μm): Fe-LRT (72% of the particles were smaller than 1 μm), Fe-SUL (99%) and Fe-V (76%). Vegetative dust (Fe-P) was equally distributed (51% submicron, 49% supermicron). By contrast, mineral dust and brake dust were found more abundant in the supermicron (>1 μm) size range: 82% and 73%, respectively, as found in previous studies[5,6].

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

By contrast , local sources were found to contribute only in small percentages to Fe aerosol particle concentrations. In urban areas, local road traffic is recognised as an important source of particulate matter (PM). Numerous studies have been conducted regarding traffic-emitted pollutants, with most investigations focusing on exhaust emissions. The most important direct emission sources are the wear of tyres, brakes, and road surfaces. None of the six Fe-containing particle types detected at the two road sites used in this study correlated temporally with the traffic counts. Meteorological data was examined for correlation with aerosol types. However, only a weak correlation between brake wear (Fe-Brake) and wind speed (R^2 = 0.25 and 0.41 at LND and BCN, respectively) was observed. As expected, mineral dust was found to be a major source of Fe-particles in both Barcelona and London. However, an interesting finding of this work is that at the heavily trafficked London road site, brake wear was found to contribute a higher percentage by number (17%) than mineral dust (8%). Another minor anthropogenic source containing iron was associated with the marine transport sector (ATOFMS Fe-V), which is especially polluting due to the use of low-quality residual fuels containing high amounts of sulphur and heavy metals. Concentrations of V are elevated in the Mediterranean region owing to increased consumption of fuel oil for power generation, shipping and industrial emissions[66,67]. In this study the ATOFMS Fe-V particle type was found to be highly correlated with Fe-LRT (temporal $R^2 = 0.85$), suggesting that this particle type is also primarily related to long range transport rather than to local shipping from the nearby ports of Barcelona and London. With regards to other combustion sources, it is important to recognise that particles associated with biomass burning/coal combustion contribute only 4-13% of the particles sampled at the two European sites. This is in profound contrast to studies of the same type conducted in Asia, where comparing the chemical composition and spatial distribution of iron within ambient particles and standard Asian mineral dust, it was determined that the main source of field collected atmospheric Fe-containing particles was coal combustion.[36,37]

One limitation of this study is that the ATOFMS uses a laser desorption/ionization (LDI). Such process is heavily influenced by particle size, morphology and matrix composition, since these will influence energy transfer from the laser beam to the particle, vaporization of the particle and ion formation in the vaporization plume. As a result, whilst the ATOFMS can provide the precise aerodynamic diameter of individual particles, the chemical information obtained by this type of single particle mass spectrometry can only be treated as qualitative, or semi-quantitative after a complex calibration[68]. Luckily, there are a number of filter-based off line studies that have focused on the aerosol mass source apportionment of Fe in the PM_1 and $PM_{2.5}$ aerosol size fraction. Interestingly, in the coarse fraction (PM > 2.5 μm) Fe is usually associated with mineral dust, road dust and traffic related matter. However, the source distribution of Fe in the finer size fraction is not clear at all. In the city of Barcelona, Amato et al.[67] reported that major sources of $PM_{2.5}$ Fe are due to mineral and industrial activity. However, about 15-30% of the PM_1 and $PM_{2.5}$ Fe was attributed to secondary more aged material not of local origin. Cusack et al.[8] reported a detailed source apportionment of PM_1 at a regional background site in the western Mediterranean. It was found that about 45% of PM_1 iron was associated with secondary sulphate and secondary organic aerosol.

Perrone et al.[9] reported almost two years of data of $PM_{2.5}$ and PM_1 samples collected at a central Mediterranean site. It was found that 60% of the aerosol mass $PM_{2.5}$ occurred in the PM_1 range . The PM source identification showed that Fe in the $PM_{2.5}$ was distributed almost equally between four sources: reacted dust, heavy oil combustion, secondary marine and traffic. Within the PM_1 mass region, Perrone et al.[9] reported that about 60% of the Fe was related to long range transport sources: nitrate with reacted dust, secondary marine and ammonium sulphate. During the same SAPUSS field campaign used in this work, Dall´Osto[7] reported hourly metal concentrations. $PM_{2.5}$ Fe was higher at the road site than the urban background site, stressing the importance of traffic activities. About 70% was related to non-exhaust traffic activity, and the rest to industry (about 10%) and dust (about 20%). However, nitrate was not detectable by the analytical technique used (PIXE), so the results from this study cannot readily be compared. Fewer studies are available in London, although recently Visser et al.[10] reported a very detailed study of the kerb and urban increment of highly time-resolved trace elements in PM_{10}, $PM_{2.5}$ and PM_1 aerosol in London. While 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 background sites (5.5 and 5.6), suggesting the higher importance of fine Fe-containing aerosols away from traffic sources. Indeed - regardless of the local impact of vehicles at each monitoring site - this study shows that most of the fine Fe-containing particles detected are related to long range transport.

Another interesting finding is that the major particle type characterised in this study - related to regional and long range transport - is internally mixed with nitrate. Our results are in profound contrast with previous important work carried out in Asia, where Fe-containing particles were found to be internally mixed with secondary species such as sulphate, soot, and organic carbon, but not nitrate.[21,36,37] . It is relevant that within the European Union (EU), in the last decades much lower SO_2 levels are being recorded following strict implementation of industrial pollution controls[69]. EU abatement of traffic related NO_x levels is still required to maintain levels within international standards[69]. Control actions in Asia have also been taken, although their effectiveness is outweighed by increased energy demand, with larger amount of SO_2 from coal relative to Europe[70-71]. The fact that our detected long range transport Fe-containing aerosols are internally mixed with nitrate is not surprising given the higher amount of NO_x relative to SO_2 in the urban atmosphere, whereas the latter has much higher concentrations in Asia. As regards of the seasonality of the studied main Fe particle type (Fe-LRT), the two field studies herein reported were carried out in spring (London) and fall (Barcelona). Whilst previous analysis show a reduction due to evaporation of nitrate during warm summer months, the evolution of nitrate can be heavily influenced by meteorological factors[72]. Given the likely urban anthropogenic source of fine iron-nitrate particles, we speculate the mixing state may not change dramatically across most of the year.

We looked at iron containing particles sampled by ATOFMS at other European sites. A previous study of the size distributions and the chemical characterization of airborne particles in the vicinity of a large integrated European steelworks[73] found that Fe-rich particles were mainly related to emissions from the blast furnace as a result of furnace tapping and slag quenching operations. It was found that Fe-rich particles are internally mixed with nitrate (and very little sulphate), reporting mass spectra similar to those shown in Figure 1a, suggesting a contribution of this source to the ATOFMS Fe-LRT particle type. Data sets from two other studies carried out at Mace Head, Ireland[26] and in the Po Valley, Italy[74] were queried for fine Fe-containing particles. It was found that most of the fine Fe containing particles are of anthropogenic origin and internally mixed with nitrate - consistent with this study. However, Fe-containing particles represented less than 0.5% of the total sampled particles.

We did not study the solubility of the detected particles. Generally, Fe-nitrate chemical species are usually more soluble than Fe-sulphate species. Baker and Jickells[18] reported an inverse relationship between dust mass concentration and FFS, arguing that the greater solubility at lower dust mass concentration could be due to a larger surface area to volume ratio of the finer dust particles.

However, later studies[17-19] reported that the size dependence of the FFS can at most explain a small part of the measured variability in FFS in atmospheric aerosol samples. Overall, natural Fe-dust is generally found in the coarser mode than anthropogenic urban related Fe-dust[22]. While no conclusions can be drawn on aerosol solubility, this study shows that the main type of fine Fe-containing particles in the urban atmosphere are internally mixed with nitrate, hence of different chemical composition of natural Fe-dust. Additionally, it is important to remember that while sulphate is not considered a nutrient for marine microorganisms, nitrate is a key one, alongside iron. Atmospheric reactive nitrogen is mainly derived from anthropogenic combustion or agricultural sources in densely populated regions throughout the world.[30] The supply of new nutrients to the ocean from external sources such as atmospheric deposition has been extensively addressed in iron-limited High Nutrient-Low Chlorophyll (HNLC) regions,[31] most of which receive low atmospheric inputs at the present time.[32] How the ocean responds to pulses of deposition - as either transient or long-term impacts on diversity of the natural assemblage and/or carbon export - is not obvious. Guieu et al.[58] recently reviewed the significance of the episodic nature of atmospheric deposition to low nutrient LNLC regions. Most of the experimental studies presented used desert dust but few considered its solubility and hence bioavailability. This is particularly important because desert dusts derived from soils contain very little soluble nitrogen whereas “atmospherically processed dust” is rich in nitrogen. It was stressed that differences in the source of the material used (e.g., soil vs. locally collected aerosols), related composition, and solubility may partially explain the observed variability in response. Deposition of iron, nitrogen, phosphorus and organic matter has increased considerably since preindustrial times[30] and nitrogen could further slightly increase in the future (Guieu et al.[32] and ref. included). The present study shows that anthropogenic Fe-containing particles also contain nitrate, and the interactive effects and the possible synergy of both nutrients is not currently accounted for in ocean global biogeochemical cycles. The solubility of Fe in atmospheric aerosols, model soils, and desert samples has been investigated thoroughly in various ocean and atmospheric environments during the past decade,[17-19] illustrating the complex nature of iron solubility in atmospheric aerosols. This study shows that the majority of fine Fe-containing particles collected in urban European environment are internally mixed with nitrate, and it is important to keep this in mind when studying both the health effects of urban aerosol and the impact of iron in LNLC-HNLC oceanic regions impacted by long range transport of European anthropogenic aerosol.

ACKNOWLEDGMENTS

Authors thank David Green from King’s College London for providing vehicular traffic flow data in London and FP7-PEOPLE-2009-IEF, Project number 254773, SAPUSS – Solving Aerosol Problems Using Synergistic Strategies (Marie Curie Actions – Intra European Fellowships, Manuel Dall’Osto). This study was also supported by research projects from the D.G. de Calidad y Evaluacion Ambiental (Spanish Ministry of the Environment) and the UK National Centre for Atmospheric Science. Dr. Xavier Querol´s group is also acknowledged for field support.

REFERENCES

(1) Pope, C. A.; Dockery, D. W. Health effects of fine particulate air pollution: lines that connect. *J. Air Waste Manage. Assoc.* **2006**, *56*, 709-742.

(2) IPCC, 2007. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K. B.; Tignor, M.; Miller, H. L. *Cambridge University Press* **2007**, Cambridge, United Kingdom and New York, NY, USA, 996 pp.

(3) Jickells, T. D.; An, Z. S.; Andersen, K.K.; Baker, A.R.; Bergametti, G.; Brooks, N.; Cao, J. J; Boyd, P.W, et al. Torres, R. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **2005**, *308*, 6-71.

(4) Lough, G. C., Schauer, J.;J.; Park, J.-S.; Shafter, M. M.; Deminter, J. T.; Weinstein, J. P. Emissions of metals associated with motor vehicle roadways. *Environ. Sci. Technol.* **2005**, *39*, 826-836.

(5) Harrison, R. M.; Jones, A. M.; Lawrence, R. G. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. *Atmos. Environ.* **2003** *37*, 4927-4933.

(6) Gietl, J. K.; Lawrence, R.; Thorpe, A. J.; Harrison, R .M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* **2010**, *44*, 141-146,.

(7) Dall'Osto, M.; Querol, X.; Amato, F.; Karanasiou, A.; Lucarelli, F.; Nava, S.; Calzolai, G.; Chiari, M. Hourly elemental concentrations in PM2.5 aerosols sampled simultaneously at urban background and road site during SAPUSS – diurnal variations and PMF receptor modelling. *Atmos. Chem. Phys.* **2013**, *13*, 4375-4392.

(8) Cusack, M.; Pérez, N.; Pey, J., Alastuey; A.; Querol, X. Source apportionment of fine PM and sub-micron particle number concentrations at a regional background site in the western Mediterranean: a 2.5 year study. *Atmos. Chem. Phys.* **2013**, *13*, 5173-5187.

(9) Perrone M. R.; Becagli, S.; Garcia Orza, J. A.; Vecchi, R.; Dinoi, A.; Udisti, R.; Cabello, M. The impact of long-range-transport on PM1 and PM2.5 at a Central Mediterranean site. *Atmos. Environ.* **2013**, *71*, 176-186.

(10) Visser, S.; Slowik, J. G.; Furger, M.; Zotter, P.; Bukowiecki, N.; Dressler, R.; Flechsig, U.; Appel, K, et al. Kerb and urban increment of highly time-resolved trace elements in PM10, PM2.5 and PM1.0 winter aerosol in London during ClearfLo 2012. *Atmos. Chem. Phys.* **2015**, *15*, 2367-2386.

(11) Donaldson, K.; Brown, D. M.; Mitchell, C.; Dineva, M.; Beswick,P. H.; Gilmour, P.; MacNee, W. Free radical activity of PM10: Iron-mediated generation of hydroxyl radicals. *Environ. Health Perspect.* **1997**, *105*, 1285-1290.

(12) Birmili, W.; Allen, A. G.; Bary, F.; Harrison, R. M. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environ. Sci. Technol.* **2006**, *40*, 1144-1153.

(13) Lin, C.-C.; Chen, S.-J.; Huang, K.-L.; Hwang,W.-I.; Chang-Chien, G.-P.; Lin,W.-Y. Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road. *Environ. Sci. Technol.* **2005**, *39*, 8113-8122.

(14) Costa, D.L.; Dreher, K. L. Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animalmodels. *Environ. Health Perspect.* **1997**, *105*, 1053-1060.

(15) See, S. W.; Wang, Y. H.; Balasubramanian, R. Contrasting reactive oxygen species and transition metal concentrations in combustion aerosols. *Environ. Res.* **2007**, *103*, 317-324

(16) Falkowski, P. G;, Barber, R. T.; Smetacek, V. V. Biogeochemical controls and feedbacks on ocean primary production . *Science* **1998**, *281*, 200-206.

(17) Shi, Z. B.; Krom, M. D.; Jickells, T. D.; Bonneville, S.; Carslaw, K. S.; Mihalopoulos, N.; Baker, A. R.; Benning, L. G. Impacts on iron solubility in the mineral dust by processes in the source region and the atmosphere: A review. - *Aeolian Res.* **2012**, *5*, 21-42.

(18) Baker, A. R.; Jickells, T. D. Mineral particle size as a control on aerosol iron solubility. *Geophys. Res. Lett.* **2006**, *33*, L17608. http://dx.doi.org/10.1029/2006GL026557.

(19) Baker, A .R.; Croot, P. L. Atmospheric and marine controls on aerosol iron solubility in seawater. *Mar. Chem.* **2010**, *120*, 4-13.

(20) Luo, C.; Mahowald, N.; Bond, T.; Chuang, P. Y.; Artaxo, P.; Siefert, R.; Chen, Y.; Schauer, J. Combustion iron distribution and deposition. *Glob. Biogeochem. Cycle* **2008**, **22**, GB1012, doi:10.1029/2007GB002964.

(21) Moffet, R. C.; Furutani, H.; Rödel, T. C.; Henn, T. R.; Sprau, P. O.; Laskin, A.; Uematsu, M.; Gilles, M. K. Iron speciation and mixing in single aerosol particles from the Asian continental outflow. *J. Geophys. Res.* **2012**, *117*, D07204, doi:10.1029/ 2011JD016746.

(22) Thorpe, A., Harrison, R.M., 2008. Sources and properties of non-exhaust particulate matter from road traffic: a review. The Science of the Total Environment. doi:10.1016/j.scitotenv.2008.06.007.

(23) Schulz, M., Prospero, J., Baker, A., Dentener, F., Ickes, L., Liss, P., Mahowald, N., Nickovic, S et al 2012. The atmospheric transport and deposition of mineral aerosols to the ocean: implications for reseach needs. Environ. Sci. Technol. 46, 10390–10404 (doi:

(24) Rodriguez, S., Torres, C., Guerra, J.C., Cuevas, E., 2004. Transport pathways of ozone to marine and free-tropospheric sites in Tenerife, Canary Islands. Atmospheric Environment 38, 4733–4747

(25) Cavalli, F; Facchini, MC; Decesari, S; Mircea, M; Emblico, L; Fuzzi, S; Ceburnis, D; Yoon, et al Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic. 2004. J. Geophys. Res., 109, D24215, doi:10.1029/2004JD005137

(26) Dall'Osto, M., Ceburnis, D., Martucci, G., Bialek, J., Dupuy, R., Jennings, S. G., Berresheim, H., Wenger, et al. Aerosol properties associated with air masses arriving into the North East

Atlantic during the 2008 Mace Head EUCAARI intensive observing period: an overview, Atmos. Chem. Phys., 10, 8413-8435, doi:10.5194/acp-10-8413-2010, 2010.

(27) Jordi, A., Basterretxea, G., Tovar-Sanchez, A., Alastuey, A., and Querol, X.: Copper aerosols inhibit phytoplankton growth in the Mediterranean Sea, Proc. Natl. Acad. Sci. USA **2012**, *109*, 21246– 21249, doi:10.1073/pnas.1207567110.

(28) Guieu, C., et al. (2014), The significance of the episodic nature of atmospheric deposition to Low Nutrient Low Chlorophyll regions, *Global Biogeochem. Cycles* **2014** *28*, 1179–1198, doi:10.1002/ 2014GB004852.

(29) Laskin, A.; Laskin, J.; Nizkorodov, S. A. Mass spectrometric approaches for chemical characterisation of atmospheric aerosols: critical review of the most recent advances. *Environ. Chem.* **2012**, *9*, 163-189.

(30) Duce, R. A.; La Roche, J.; Altieri, K.; Arrigo, K. R.; Baker, A. R.; Capone, D.G.; Cornell, S.; Dentener, F, et al. Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* **2008**, *320*, 893-897.

(31) Boyd, P. W.; Jickells, T.; Law, C. S.; Blain, S.; Boyle, E. A.; Buesseler, K. O.; Coale, K. H.; Cullen, J. J, et al. A synthesis of mesoscale iron enrichment experiments 1993–2005: Key findings and implications for ocean biogeochemistry, *Science* **2007**, *315*, 612-617.

(32) Guieu C. and Shevchenko V.P, “Dust in the Ocean,” in Encyclopedia of Marine Geosciences (Springer, Verlag, Dordrecht, 2015). doi: 10.1007/97,94-007, 6644-0-56-3

(33) Chen, Y.; Shah, N.; Huggins, F.E.; Huffman, G.P. Characterization of ambient airborne particles by energy-filtered transmission electron microscopy. *Aerosol Sci. Technol.* **2005**, *39*, 509-518.

(34) Adachi, K.; Buseck, P. R. Hosted and free-floating metal-bearing atmospheric nanoparticles in Mexico City. *Environ. Sci. Technol.* **2010**, *44*, 2299-2304.

(35) Smith, S.; Ward, M.; Lin, R.; Brydson, E.; Dall’Osto, M; Harrison, R.M. Comparative Study of Single Particle Characterisation by Transmission Electron Microscopy and Time-of-Flight Aerosol Mass Spectrometry in the London Atmosphere. *Atmos. Environ.* **2012**, *62*, 400-407.

(36) Furutani, H.; Jung, J.; Miura, K.; Takami, A.; Kato, S.; Kajii, Y.; Uematsu, M. Single-particle chemical characterization and source apportionment of iron-containing atmospheric aerosols in Asian outflow. *J. Geophys. Res.* **2011**, *116*, D18204, doi:10.1029/2011JD015867.

(37) Zhang, G.; Bi, X.; Lou, S.; Li, L.; Wang, H.;Wang, X.; Zhou, Z.; Sheng, G.; Fu, J.; Chen C. Source and mixing state of iron-containing particles in Shanghai by individual particle analysis. *Chemosphere* **2014**, *95*, 9-16.

(38) Hu Y.; Lin J.; Zhang S.; Kong L.; Fu H.; Chen J. Identification of the typical metal particles among haze, fog, and clear episodes in the Beijing atmosphere. *Sci. Total Environ.* **2015**, *511*, 369-80.

(39) Querol, X.; Alastuey, A.; Ruiz, C.R.; Artinano, B.; Hansson, H.C.; Harrison, R.M.; Buringh, E.; ten Brink, H.M.; Lutz, M.; Bruckmann, P.; Straehl, P.; Schneider, J. Speciation and origin of PM10 and PM2.5 in selected European cities. *Atmos. Environ.* **2004**, *38*, 6547-6555.

(40) Mihalopoulos, N.; Kallos, G.; Kleanthous S. African dust contributions to mean ambient PM10 mass-levels across the Mediterranean Basin. *Atmos. Environ.* **2009**, *43*, 4266-4277.

(41) Revuelta, M. A.; Harrison, R. M.; Núñez, L.; Gomez-Moreno F. J.; Pujadas, M.; Artíñano B. Comparison of temporal features of sulphate and nitrate at urban and rural sites in Spain and the UK. *Atmos. Environ.* **2012**, *60*, 383-391.

(42) Putaud, J. P.; Van Dingenen, R.; Alastuey, A.; Bauer, H.; Birmili,W.; Cyrys, J.; Flentje, H.; Fuzzi, S.; et al. A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ.* **2010**, *44*, 1308-1320.

(43) Dall'Osto, M.; Querol, X.; Alastuey, A.; Minguillon, M. C.; Alier, M.; Amato, F.; Brines, M.; Cusack, M, et al. Presenting SAPUSS: Solving Aerosol Problem by Using Synergistic Strategies in Barcelona, Spain. *Atmos. Chem. Phys.* **2013a**, *13*, 8991-9019.

(44) Harrison, R. M.; Dall'Osto, M.; Beddows, D. C. S.; Thorpe, A. J.; Bloss, W. J.; Allan, J. D.; Coe, H.; Dorsey, J. R.; et al Atmospheric chemistry and physics in the atmosphere of a developed megacity (London): an overview of the REPARTEE experiment and its conclusions. *Atmos. Chem. Phys.* **2012**, *12*, 3065-3114.

(45) Wroth, C.; Wiles, A. Key Population and Vital Statistics, Series VS No 34, PPI no 30, 2007 Data, Office for National Statistics, http://www.ons.gov.uk/ons/rel/kpvs/key-population-and-vital-statistics/no--34--2007-edition/index.html (last accessed 13 August 2015).

(46) Giorio, C.; Tapparo, A.; Dall'Osto, M.; Beddows, D.C.; Esser-Gietl, J.K.; Healy, R.M.; Harrison, R.M. Local and regional components of aerosol in a heavily trafficked street canyon in central London derived from PMF and cluster analysis of single-particle ATOFMS spectra. *Environ Sci Technol.* **2015**, *49*, 3330-3340.

(47) Gard, E.; Mayer, J. E.; Morrical, B. D.; Dienes, T.; Fergenson, D. P.; Prather K. A. Real-time analysis of individual atmospheric aerosol particles: Design and performance of a portable ATOFMS. *Anal. Chem.* **1997**, *69*, 4083-4091,.

(48) Pratt, K. A.; Prather, K. A. Mass spectrometry of atmospheric aerosols – Recent developments and applications, Part II: On-line mass spectrometry techniques. *Mass Spectrom. Rev.* **2012**, *31*, 17-48,

(49) Spencer, M. T.; Shields, L. G.; Sodeman, D. A.; Toner, S. M.; Prather K. A. Comparison of oil and fuel particle chemical signatures with particle emissions from heavy and light duty vehicles. *Atmos. Environ.* **2006**, *40*, 5224-5235.

(50) Song, X. H.; Hopke, P. K.; Fergenson, D. P.; Prather, K. A. Classification of single particles analyzed by ATOFMS using an artificial neural network, ART-2A. *Anal. Chem.* **1999**, *71*, 860-865.

(51) Dall'Osto, M.; Harrison R. M. Chemical Characterisation of single airborne particles in Athens (Greece) by ATOFMS. *Atmos. Environ*. **2006**, *40*, 7614-7631.

(52) Rajkumar, W.S.; Chang, A.S. Suspended particulate matter concentrations along the East-West Corridor, Trinidad, West Indies. *Atmos. Environ.* **2000**, *34*, 1181-1187.

(53) Rodriguez, S.; Querol, X.; Alastuey, A.; Kallos, G.; Kakaliagou, O. Saharan dust contributions to PM10 and TSP levels in Southern and Eastern Spain. *Atmos. Environ.* **2001**, *35*, 2433-2447.

(54) Dall'Osto, M.; Beddows, D. C. S.; Kinnersley, R. P.; Harrison, R. M.; Donovan, R. J.; Heal, M. R. Characterization of individual airborne particles by using Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) at Mace Head, Ireland. *J. Geophys. Res.* **2004**, *109*, D21302, doi:10.1029/2004/JD004747.

(55) Beddows, D. C. S.; Dall'Osto, M.; Fielding, M.-J.; Harrison, R. M. Detection of brake wear aerosols by aerosol time-of-flight mass spectrometry. In preparation, **2015**.

(56) Pattanaik, S.; Huggins, F. E.; Huffman, G. P.; Linak, W. P.; Miller, C. A. XAFS studies of nickel and sulfur speciation in residual oil fly-ash particulate matters (ROFA PM). *Environ. Sci. Technol.* **2007**, *41*, 1104-1110.

(57) Ault, A.P.; Gaston, C.J.; Wang, Y.; Dominguez, G.; Thiemens, M.H.; Prather, K.A. Characterization of the single particle mixing state of individual ship plume events measured at the port of Los Angeles. *Environ. Sci. Technol.* **2010**, *44*, 1954-1961.

(58) Ault, A. P.; Moore, M. J.; Furutani, H.; Prather, K. A. Impact of emissions from the Los Angeles port region on San Diego air quality during regional transport events. *Environ. Sci. Technol.* **2009**, *43*, 3500-3506.

(59) Sullivan, R. C.; Prather, K. A. Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation. *Anal. Chem.* **2005**, *77*, 3861-3885,

(60) Guazzotti, S. A.; Suess, D. T.; Coffee, K. R.; Quinn, P. K.; Bates, T. S.; Wisthaler, A.; Hansel, A.; Ball, W. P.; et al. Characterization of carbonaceous aerosols outflow from India and Arabia: biomass/biofuel burning and fossil fuel combustion. *J.Geophys. Res.-Atmospheres* **2003**,*108*, D15, 4485, doi:10.1029/2002JD003277.

(61) Fergenson, D. P.; Pitesky, M. E.; Tobias, H. J.; Steele, P. T.; Czerwieniec, G. A.; Russell, D. H.; Lebrilla, C. B.; Horn, J, et al.Reagentless Detection and Classification of Individual Bioaerosol Particles in Seconds. *Anal. Chem.* **2004**, *76*, 373-378.

(62) Vogt, R.; Kirchner, U.; Scheer, V.K.; Hinz, P.; Trimborn; A.; Spengler, B. Identification of diesel exhaust particles at an Autobahn, urban and rural location using single-particle mass spectrometry. *J. Aerosol Sci*. **2003**, *34*, 319-337.

(63) Silva, P. J.; Liu, D.-Y.; Noble, C. A.; Prather, K. A. Size and chemical characterization of individual particles resulting from biomass burning of local Southern California species. *Environ. Sci. Technol.* **1999**, *33*, 3068-3076.

(64) Dall'Osto, M., Harrison, R. M., Beddows, D. C. S., Freney, E. J., Heal, M. R., and Donovan R. J.: Single-particle detection efficiencies of aerosol time-of-flight mass spectrometry during the North Atlantic marine boundary layer experiment, Environ. Sci. Technol., 40, 5029–5035, 2006.

(65) Charron, A.; Harris, R.; Quincey, P. What are the sources and conditions responsible for exceedances of the 24h PM10 limit value (50 µg m^{-3}) at a heavily trafficked London site? *Atmos. Environ.* **2007**, *41*, 1960-1975.

(66) Viana, M.; Amato, F.; Alastuey, A.; Querol, X.; Saúl, G.; Herce-Garraleta, D.; Fernandez-Patier, R. Chemical tracers of particulate emissions from commercial shipping. *Environ. Sci. Technol.* **2009**, *43*, 7472-7477.

(67) Amato, F.; Pandolfi, M.; Escrig, A.; Querol, X.; Alastuey, A.; Pey, J.; Perez, N.; Hopke, P.K. Quantifying road dust resuspension in urban environment by Multilinear Engine: A comparison with PMF2. *Atmos. Environ.* **2009**, *43*, 2770-2780.

(68) Bhave, P. V.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Cass, G. R.; Prather, K. A. A field-based approach for determining ATOFMS instrument sensitivities to ammonium and nitrate. *Environ. Sci. Technol.* **2002**, *36*, 4868-4879.

(69) EEA 2007. EMEP / CORINAIR Atmospheric Emission Inventory Guidebook - 2007. European Environment Agency, 2007. http://reports.eea.europa.eu/EMEPCORINAIR5/

(70) Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., and Hayasaka, T.: An Asian emission inventory of anthropogenic emission sources for the period 1980–2020, Atmos. Chem. Phys., 7, 4419-4444, doi:10.5194/acp-7-4419-2007, 2007.

(71) Xing, J., Mathur, R., Pleim, J., Hogrefe, C., Gan, C.-M., Wong, D. C., Wei, C., Gilliam, R., Pouliot, G.: Observations and modeling of air quality trends over 1990–2010 across the Northern Hemisphere: China, the United States and Europe, Atmos. Chem. Phys., 15, 2723-2747, doi:10.5194/acp-15-2723-2015, 2015.

(72) Revuelta, M. A., Harrison, R. M., Núñez, L., Gómez-Moreno, F. J., Pujadas, M., and Artíñano, B.: Comparison of temporal features of sulphate and nitrate at urban and rural sites in Spain and the UK, Atmos. Environ., 60, 383–391, 2012.

(73) Dall'Osto, M.; Booth, M. J.; Smith, W.; Fisher, R.; Harrison R. M. A study of the size distributions and the chemical characterization of airborne particles in the vicinity of a large integrated steelworks. *Aerosol Sci. Technol.* **2008**, *42*, 981-991.

TABLE LEGEND

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

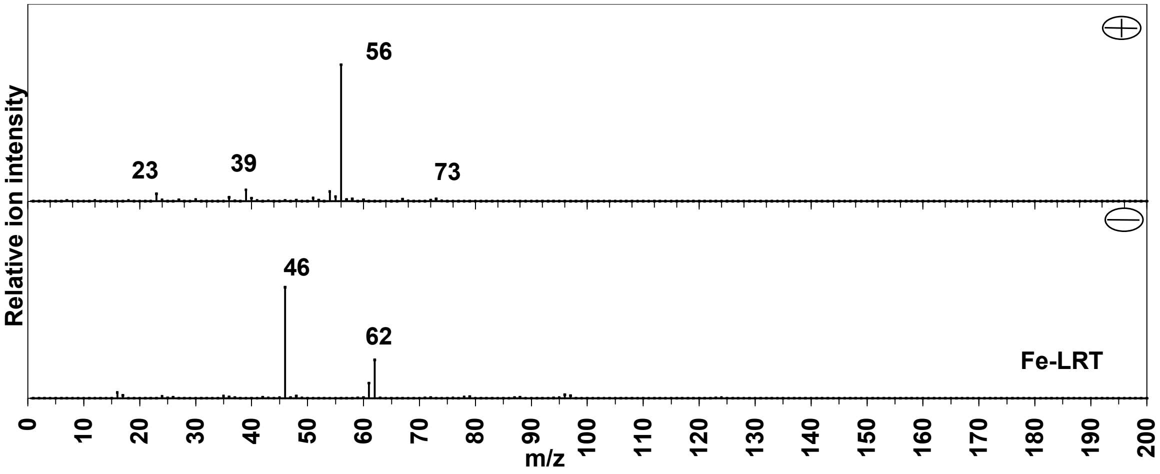
FIGURE LEGENDS

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

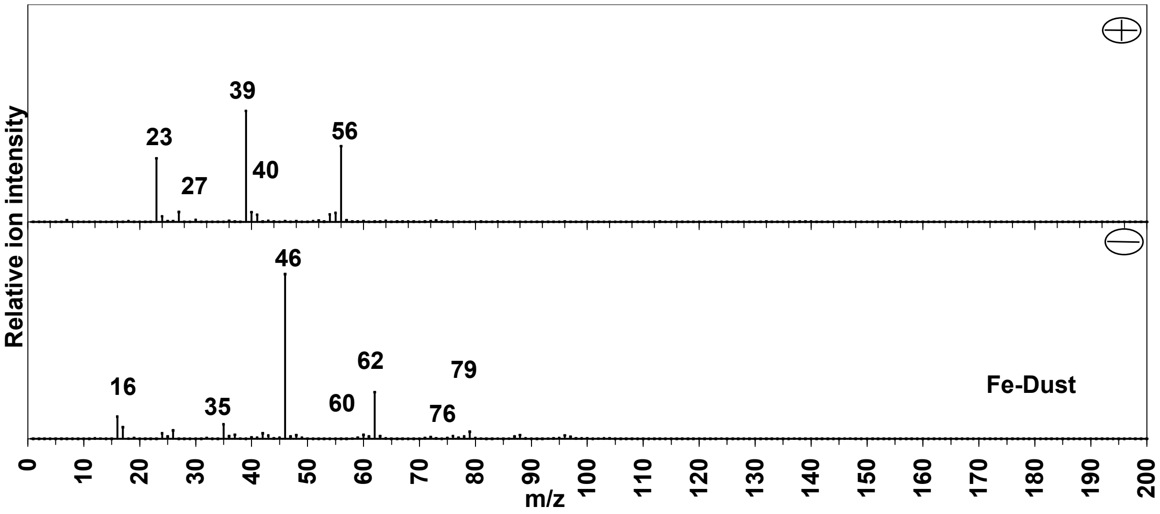
Figure 2: Size distributions of the six different particle types detected at the two European sites. It is clear that combustion Fe-SUL are in the fine mode, the nitrate-Fe in the accumulation mode, and the Fe-Brake and Fe-Dust in the coarser mode. Fe-V in the fine combustion mode, Fe-P (vegetative debris)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

Table 1: Major types of Fe-containing particles identified by the ATOFMS, and their abundance in the Barcelona (BCN) and London (LND) studies. In the text the interval of the % are given as % across the two monitoring sites (BCN and LND, i.e. Fe_LRT is 54-82%).

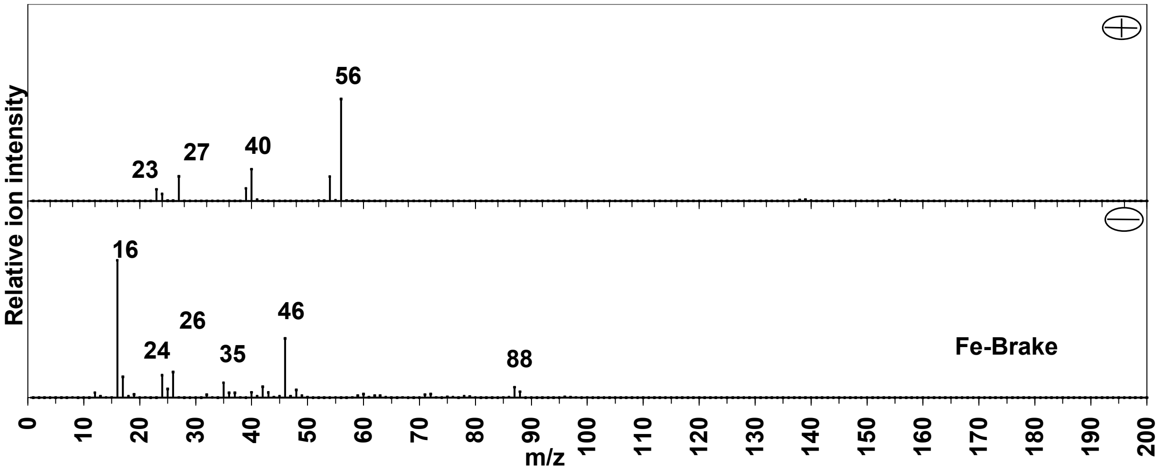
ATOFMS particle type	Total particle number		%	
	BCN	LND	BCN	LND
Fe_LRT	5221	2254	82	54
Fe_Dust	664	344	11	8
Fe_Brake	41	695	1	17
Fe_V	61	244	1	6
Fe_SUL	282	524	4	13
Fe_P	106	113	1	3
Total	6375	4174	100	100


Relative ion intensity
⊕
⊖
56
23
39
73
46
62
Fe-LRT
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
m/z

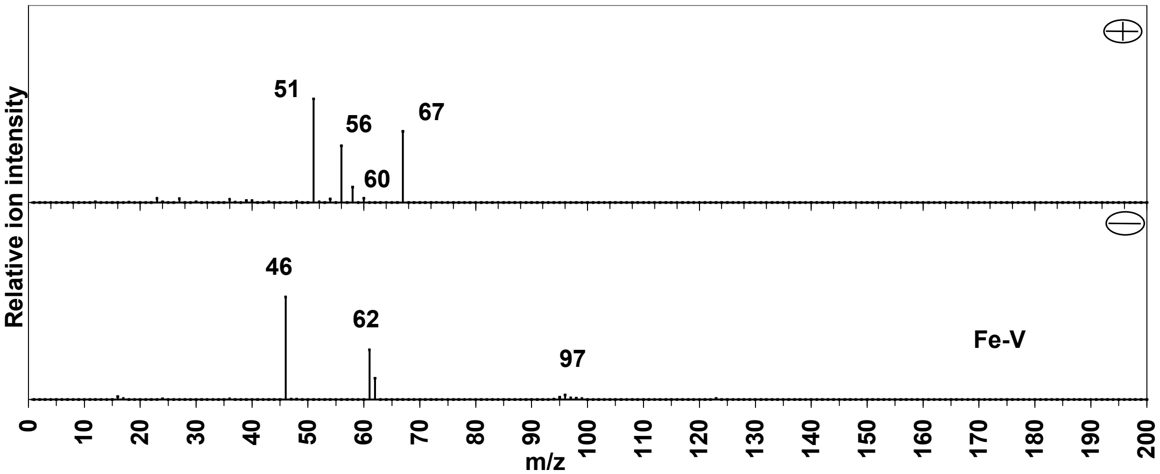
(a)


Relative ion intensity
⊕
⊖
39
23
27
40
56
46
16
35
60
62
76
79
Fe-Dust
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
m/z

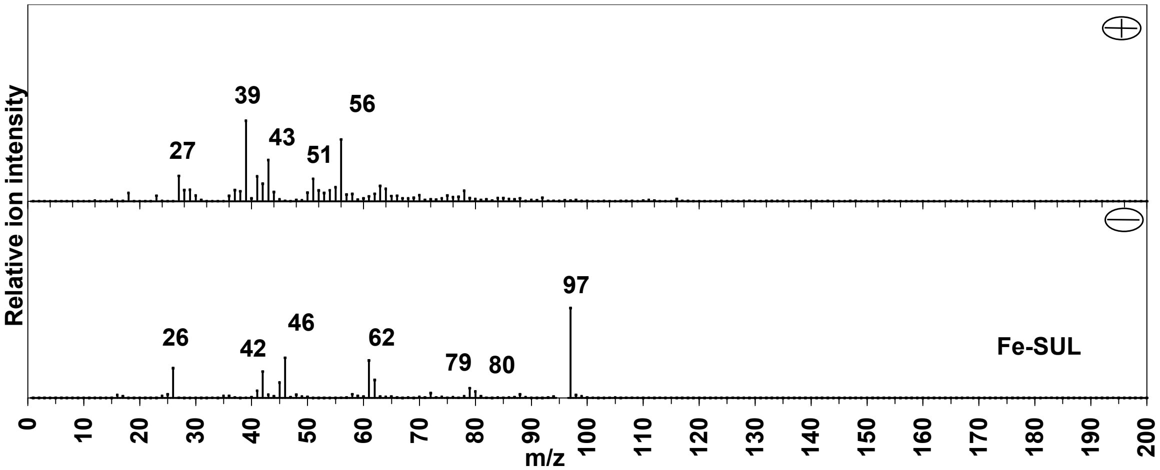
(b)


Relative ion intensity
⊕
⊖
56
23
27
40
16
24
26
35
46
88
Fe-Brake
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
m/z

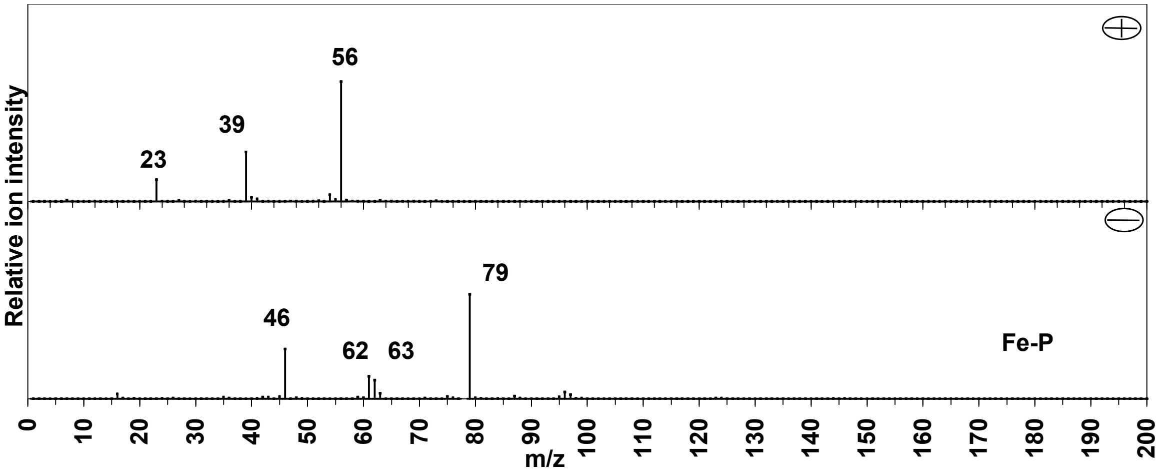
(c)



(d)



(e)



(f)

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

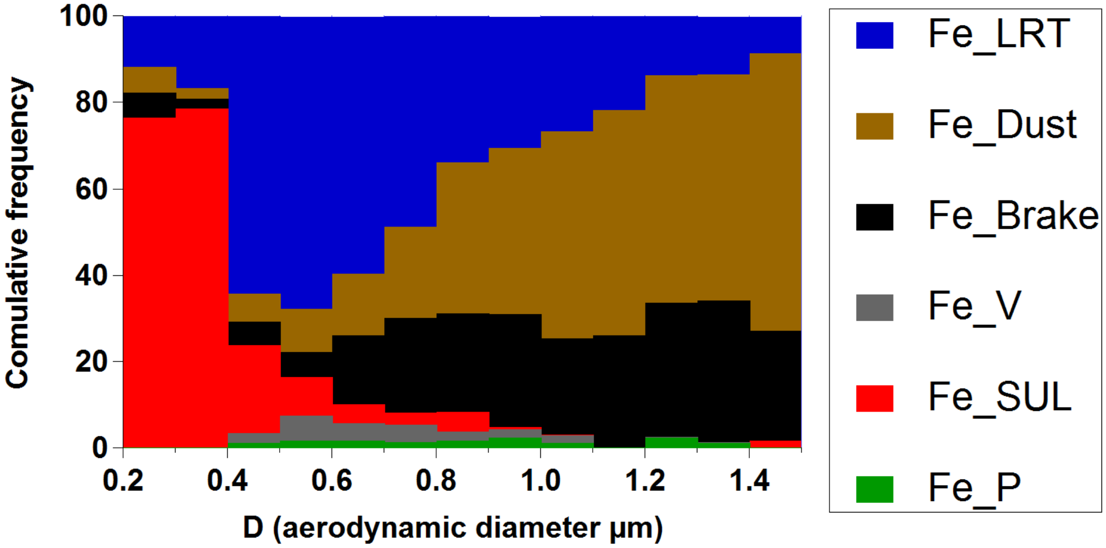


Figure 2: Size distributions of the six different particle types detected at the two European sites. It is clear that combustion Fe-SUL are in the fine mode, the nitrate-Fe in the accumulation mode, and the Fe-Brake and Fe-Dust in the coarser mode. Fe-V in the fine combustion mode, Fe-P (vegetative debris)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