

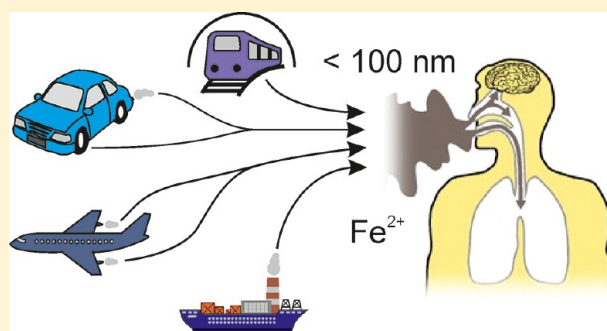
# Airborne, Vehicle-Derived Fe-Bearing Nanoparticles in the Urban Environment: A Review

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## Supporting Information

**ABSTRACT:** Airborne particulate matter poses a serious threat to human health. Exposure to nanosized ( $<0.1 \mu\text{m}$ ), vehicle-derived particulates may be hazardous due to their bioreactivity, their ability to penetrate every organ, including the brain, and their abundance in the urban atmosphere. Fe-bearing nanoparticles ( $<0.1 \mu\text{m}$ ) in urban environments may be especially important because of their pathogenicity and possible association with neurodegenerative diseases, such as Alzheimer's and Parkinson's diseases. This review examines current knowledge regarding the sources of vehicle-derived Fe-bearing nanoparticles, their chemical and mineralogical compositions, grain size distribution and potential hazard to human health. We focus on data reported for the following sources of Fe-bearing nanoparticles: exhaust emissions (both diesel and gasoline), brake wear, tire and road surface wear, resuspension of roadside dust, underground, train and tram emissions, and aircraft and shipping emissions. We identify limitations and gaps in existing knowledge as well as future challenges and perspectives for studies of airborne Fe-bearing nanoparticles.



## 1. INTRODUCTION

Exposure to airborne particulate matter (PM) is known to pose a serious threat to human health, linked with damage not only to respiratory and cardiovascular health, but also to neurodevelopment and cognitive function. Metal-bearing, nanosized ( $<0.1 \mu\text{m}$ ) particles may be especially hazardous to human health<sup>1–7</sup> because of their abundance in the urban atmosphere,<sup>8–13</sup> bioreactivity,<sup>10,14–16</sup> and their ability to reach all major organs of the human body by inhalation<sup>10,17–21</sup> and by circulation in the bloodstream.<sup>22</sup>

As evident from Figure 1, metal-bearing (e.g., Au-, Ba-, Cd-, Fe-, Mn-, Ti-bearing) particles may be translocated from the lungs to sites of vascular inflammation,<sup>22</sup> the central nervous system,<sup>23–25</sup> liver<sup>22,26</sup> and amniotic fluid.<sup>27</sup> Particles  $<200 \text{ nm}$  can access the brain directly, bypassing the blood–brain barrier, via transport through the neuronal axons of the olfactory and/or trigeminal nerves.<sup>10,24</sup> Exposure to particulate air pollution may thus cause damage to neurodevelopment and cognitive functions.<sup>10,28–33</sup> Large population-scale epidemiological studies show that living close to heavy traffic is associated with a higher incidence of dementia.<sup>33–36</sup> Other epidemiological studies in the USA and Mexico indicate that young and old subjects living in areas with high airborne PM concentrations have cognitive deficits.<sup>37–40</sup> In a magnetic resonance imaging (MRI) analysis of elderly women (age from 71 to 89 years; the Women's Health Initiative Memory Study cohort), white matter loss was increased by 1% per  $3 \mu\text{g}/\text{m}^3$  of  $\text{PM}_{2.5}$ .<sup>41</sup> Post-mortem brain samples from clinically healthy

subjects (and dogs) exposed to lifetime high pollution, while living in Mexico City<sup>10,28,30</sup> or Manchester, UK<sup>10</sup> display: (i) typical hallmarks of Alzheimer's disease (AD) pathogenesis (e.g., tau-P,  $\beta$ -amyloid deposition), (ii) inflammation, oxidative stress and DNA signaling damage;<sup>30</sup> and (iii) the abundant presence of metal-bearing NPs, including mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (magnetite) NPs, as determined by electron microscopy (EM) and magnetic analyses.<sup>10</sup> Mouse models for urban nanoparticulate air pollution show consistent induction of inflammatory responses in major brain regions<sup>42</sup> (see also Table SI 3 (Supporting Information)).

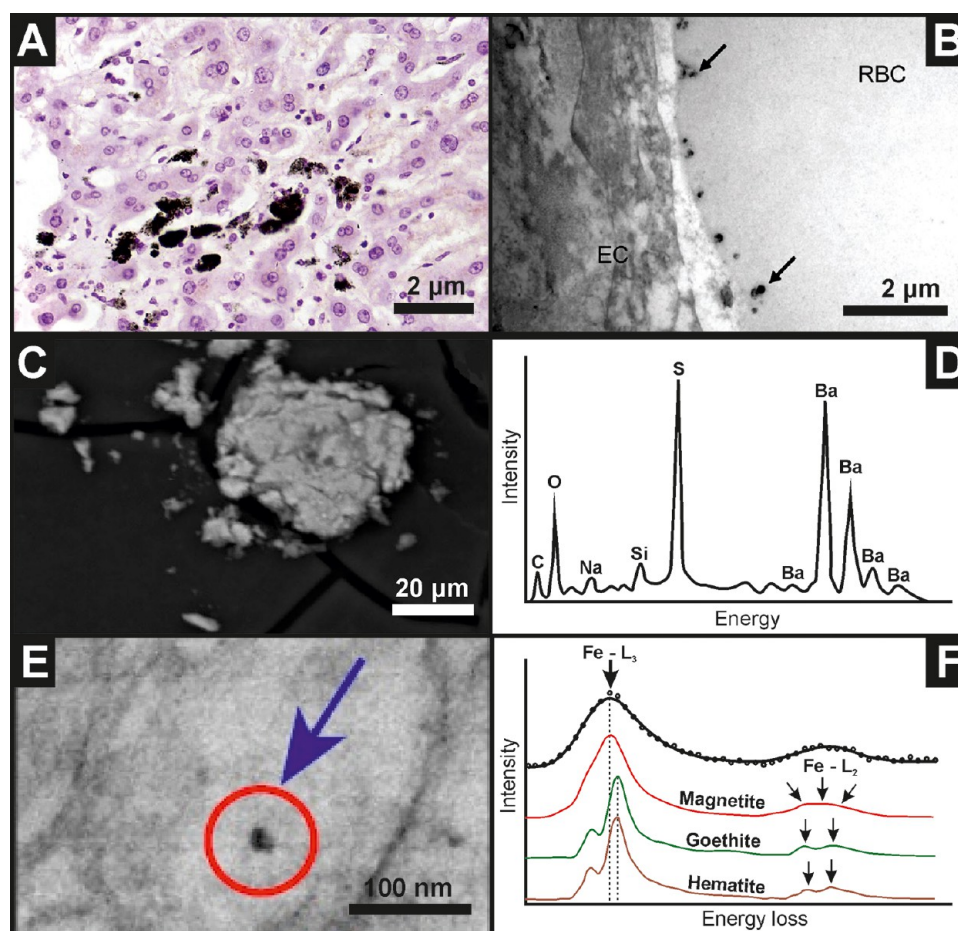
Due to their large surface area and potentially high reactivity with biomolecules and tissues, metal-bearing nanoparticles (NPs) may generate adverse health impacts related to oxidative stress, inflammation,<sup>18,19,43–47</sup> and generation of reactive oxygen species (ROS).<sup>3,48–50</sup> Exposure to bioreactive airborne NPs can occur at every life stage; in the womb,<sup>27,51</sup> as developing infants and children,<sup>37,52–56</sup> and through adulthood to terminal decline. Both the young and the elderly are particularly vulnerable to air pollution.<sup>57–62</sup> Prebirth exposures to both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  are associated with low birth weight (e.g., refs 62–65). Childhood exposures to traffic-derived PM (elemental carbon – EC, nitrogen dioxide –  $\text{NO}_2$  and PM  $<$

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**Figure 1.** Metal-bearing particles found in the human body: (A) PM in the liver of a 32 year-old male (adapted from Calderón-Garcidueñas et al.<sup>30</sup>); (B) PM spherules in a lung capillary, RBC = red blood cell; EC = endothelial cell (adapted from Calderón-Garcidueñas et al.<sup>30</sup>); (C) SEM image of Ba-bearing particles in the amniotic fluid with (D) the corresponding EDS spectrum (adapted from Barošová et al.<sup>27</sup>); (E) TEM image of magnetite NPs in frontal cortex brain tissue with (F) corresponding electron energy loss spectroscopy spectra (in black) for the rounded particle shown in E and for standard Fe oxide species (adapted from Maher et al.<sup>10</sup>).

700 nm) impair lung growth<sup>66</sup> and cognitive development.<sup>55,56</sup> These early life exposures to airborne PM can thus set in train a sequence of health problems which progressively develop through later life. Children spend more time outdoors, are more physically active, and they have an increased breathing rate and immature immune system, all of which result in a higher dosage in the respiratory tract of children compared to adults, especially in the case of NPs.<sup>67</sup> Compared to children living with clean air, those in polluted areas (e.g., Mexico City) display health problems, including systemic inflammation, and even Alzheimer's and Parkinson's hallmarks.<sup>30,37,38,52</sup>

Exposure specifically to Fe-bearing airborne NPs may be especially hazardous to human health. Fe is an essential biometal, as a component of diverse metalloproteins, from cytochromes to hemoglobin, and playing key roles in neuronal function, ranging from nerve impulse transduction to neurotransmitter synthesis and mitochondrial energy production. Fe is mobilized and stored via changes in valence, controlled by sophisticated regulatory homeostasis processes. Such processes are vital, since labile  $\text{Fe}^{2+}$ , i.e., in the unbound, redox-active state, can be toxic to living cells. In humans, nonhaem Fe is stored in a redox-inactive, oxidized ( $\text{Fe}^{3+}$ ) form as 8 nm spherical cores of ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) within the 12 nm-diameter Fe-storage protein, ferritin. However, if redox-active, ferrous ( $\text{Fe}^{2+}$ ) remains unbound and freely available, it

can catalyze the formation of ROS, including the damaging hydroxyl radical, through the Fenton reaction.<sup>68</sup>

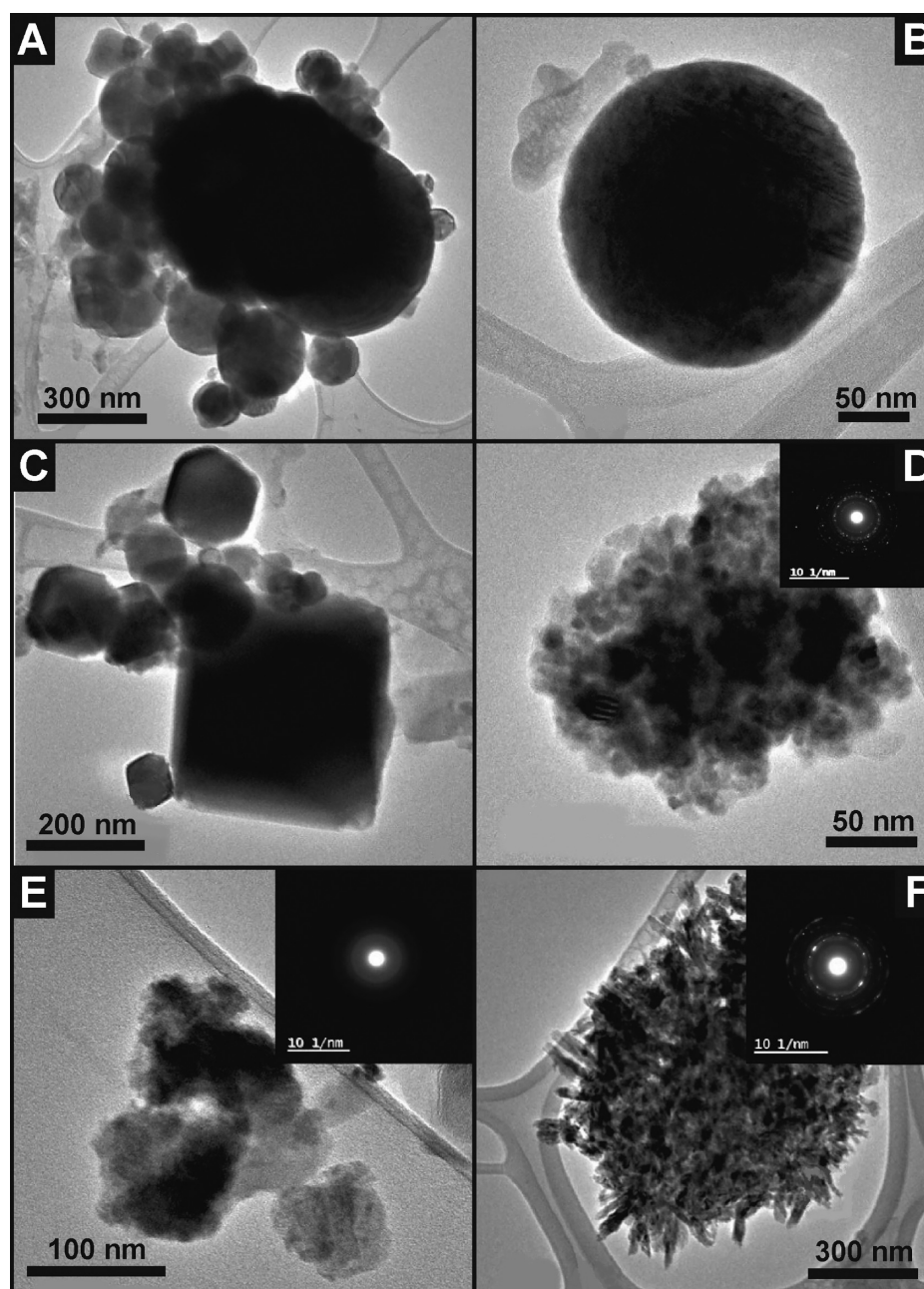
Problems with transportation and storage of Fe have been linked with a variety of diseases, including Alzheimer's, Parkinson's, Huntington's, multiple sclerosis, amyotrophic lateral sclerosis and Hallervorden–Spatz disease.<sup>68–74</sup> Some of the excess Fe found in the neurodegenerative brain occurs in the form of magnetite, a strongly magnetic, mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  oxide (see Section 12 for more details).

Given the potential risks to human health posed by airborne Fe-bearing NPs, it is timely to examine information regarding their sources, abundance and composition, in order to identify major routes of exposure, and potential pathways to removing or reducing their particle number concentrations.

## 2. IRON-BEARING NANOPARTICLES IN THE ENVIRONMENT

Fe-bearing NPs occur both abundantly and widely in the urban atmosphere.<sup>8–13</sup> Fe, in oxide, hydroxide and metallic forms, is a major contributor not only to the aerosol mass in urban environments but also, because of its abundant occurrence within primary, emitted NPs, to the particle number concentrations in urban air.

Fe has been found in high concentrations (11,000–94,000 ppm) in the submicrometer fraction of roadside PM.<sup>13</sup> Fe-



**Figure 2.** Fe-bearing NPs found in street dust: (A) aggregate of spherical magnetite particles, (B) Fe-rich fly ash, (C) magnetite particle with an octahedral shape, (D) hematite, (E) ferrihydrite, (F) goethite (adapted from Yang et al.<sup>13</sup>).

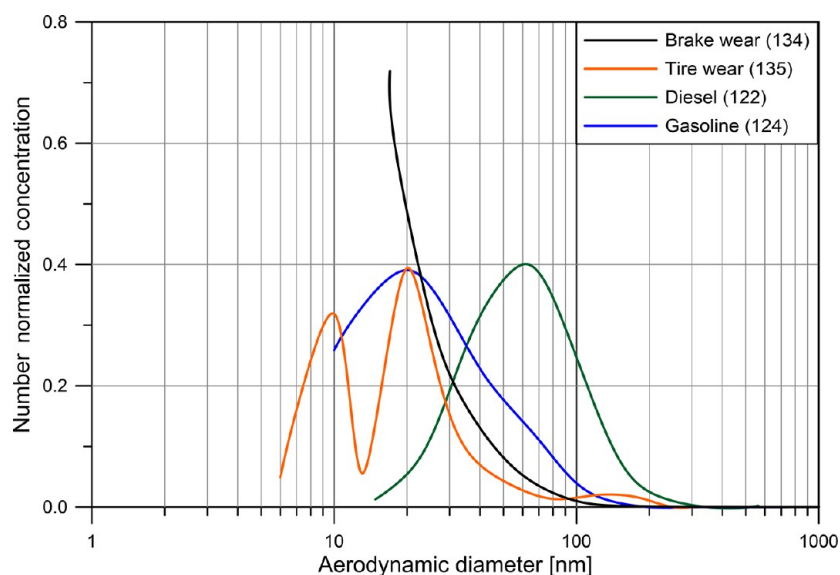
bearing NPs are frequently associated both with transition and heavy metals, including Cr, Ni, Cu, Zn, Pb, Mn.<sup>10,13,75</sup> Most of the Fe-bearing particles emitted from vehicles are ferromagnetic (*sensu lato*) Fe oxides, comprising mixtures of strongly magnetic magnetite ( $\text{Fe}_3\text{O}_4$ ), its oxidized counterpart, maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), with some metallic Fe ( $\alpha\text{-Fe}$ ) also reported.<sup>12,76–80</sup> The magnetic ordering shown by these airborne Fe-oxide particles enables their measurement and quantification using a range of concentration- and particle size-dependent magnetic analyses (see Section 11).

Magnetic particles in indoor and outdoor airborne PM can originate from a range of domestic (e.g., wood/coal burning, cigarette smoking, printer emissions), workplace, transport and industry sources (see also SI 2, Supporting Informa-

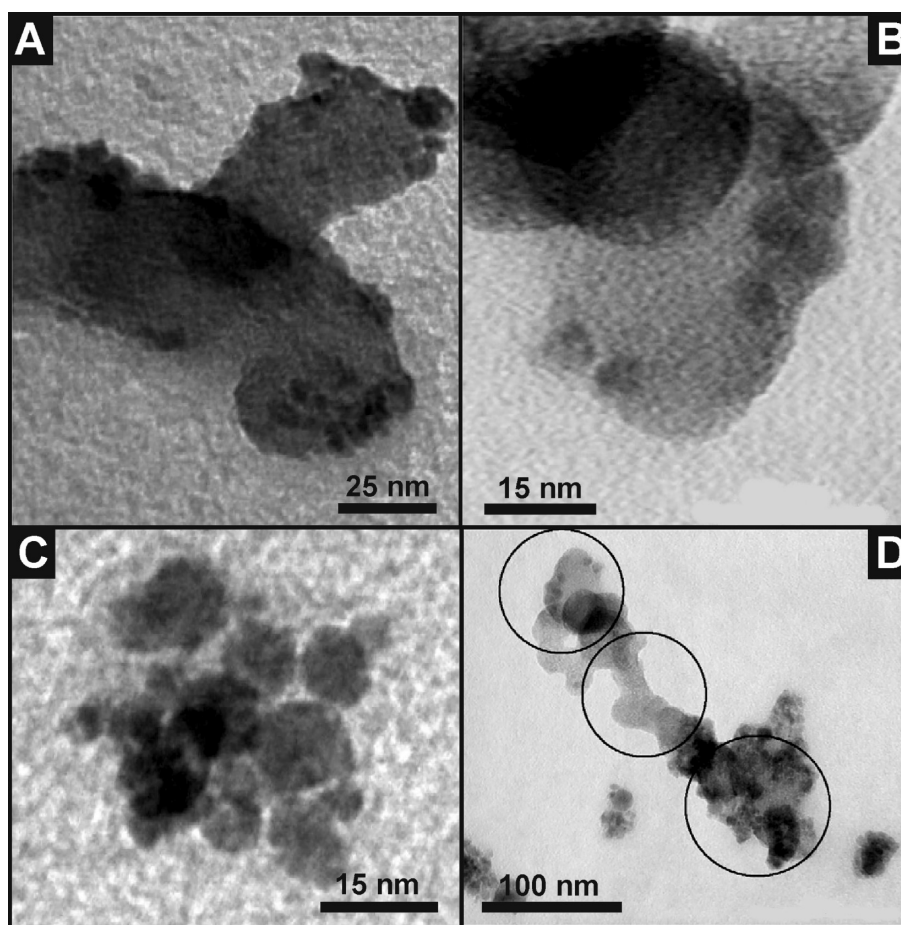
tion).<sup>78,79,81–87</sup> Such particles can occur over a great range of sizes, from several nm up to several hundred  $\mu\text{m}$ . Moreover, NPs <100 nm can agglomerate with each other and/or surround bigger particles. However, until recently, most magnetic studies have focused on PM fractions  $\geq 1 \mu\text{m}$ .

Vehicles are a major source of Fe-bearing NPs in the environment.<sup>12,13,80,86,88–96</sup> Figure 2 shows Fe-bearing NPs in street dust, variously composed of magnetite, hematite, goethite and ferrihydrite.<sup>13</sup> Vehicle-derived, Fe-bearing NPs originate from exhaust emissions, both diesel<sup>97,98</sup> and gasoline,<sup>86</sup> brake wear,<sup>96</sup> tire wear,<sup>99</sup> resuspension of roadside dust,<sup>8</sup> underground, rail and tram systems,<sup>94</sup> aircraft<sup>100</sup> and shipping emissions.<sup>91</sup>

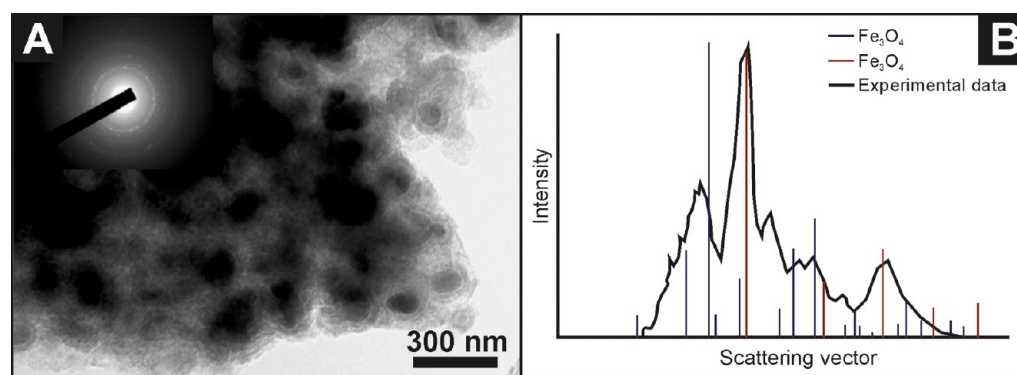




**Figure 3.** Examples of particle-size distributions for nonexhaust (brake and tire wear debris) and exhaust (diesel and gasoline) emissions. Brake wear was collected using a pin-on-disc machine (sliding speed of 13 m/s, contact pressure of 1.39 MPa, for 3 h).<sup>134</sup> Tire wear was collected using a tire test bench (inner diameter of 3.8 m, speed of 0, 30, 50 and 70 km/h).<sup>135</sup> Diesel emissions were collected using an AC electric dynamometer and the U.S. UDDS (urban dynamometer drive schedule) test cycle.<sup>122</sup> Gasoline emissions were collected using a test vehicle (acceleration from 30 to 90 km/h; hot start).<sup>124</sup>



**Figure 4.** Examples of Fe-bearing NPs in diesel emissions: (A and B) carbon agglomerates decorated with primary Fe NPs, (C) nucleated primary particles of Fe and (D) combined carbon/iron agglomerates (adapted from Miller et al.<sup>139</sup>).



**Figure 5.** (A) TEM image of NP wear particles collected during a dynamometer test and (B) electron diffraction (EDX) intensity profile (adapted from Kukutschová et al.<sup>154</sup>).

### 3. EXHAUST EMISSIONS

Exhaust emissions constitute a substantial source of Fe-bearing NPs in urban environments<sup>8,101–104</sup>). Although about 90% of tailpipe emissions is carbonaceous material, exhaust emissions contain up to 10 wt % of trace metals,<sup>105–109</sup> *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) (e.g., refs 110–112). Diesel engines also generate soot nanospheres, of between 10 and 60 nm,<sup>113,114</sup> which are often associated with Mg, Fe, Cu, Ca and Zn.<sup>104</sup> Trace metals emitted by engines include Fe, Zn, Cr, Mo, Ti, Mg, Ni, Pb, Ca, Cu, Ba, Sb, Co, Cd, V, Pt and Pd (e.g., refs 114, 115–118).

Particle size distributions (PSD) can be measured in terms of mass and number. Number-normalized PSDs are more sensitive to the presence of nanoparticles (<100 nm), which contribute most to the particle number concentrations while contributing very little to the PM mass. Number-normalized PSDs of exhaust emissions are typically bimodal, with peaks at 20–40 nm and 50–90 nm<sup>119,120</sup> or unimodal, with a peak at 10–70 nm<sup>121–124</sup> (Figure 3). Number-normalized PSDs often depend on nucleation processes and atmospheric conditions (e.g., refs 125, 126). NP numbers are also heavily influenced by the proximity of traffic (or other emission sources), especially in the case of particles of diameter <30 nm;<sup>103,127–131</sup> a point of vital importance from the epidemiological point of view as the key exposure zone for traffic is reported to be within 500 m,<sup>66,132</sup> and more specifically, within 50 m<sup>133</sup> of major roadways.

Ntziachristos et al.<sup>8</sup> studied traffic-derived PM in Los Angeles, USA and reported that Fe was a predominant metal in the <0.18  $\mu\text{m}$  fraction, accounting for 10–25% of PM<sub>0.18</sub> mass. Magnetite particles in car (diesel) exhaust emissions were first observed by Abdul-Razzaq and Gautam.<sup>97</sup> Later studies<sup>98,136–138</sup> found Fe oxide NPs in diesel emissions, and superparamagnetic (SP) NPs of magnetite and hematite<sup>86</sup> in gasoline emissions (cf. Figure 2A,B,D). Fe-bearing NPs often occur as rounded or even spherical particles, “nanospheres”, of magnetite and/or hematite, depending on combustion/heating conditions (Figure 2A,B,D).<sup>13,86,97</sup> Miller et al.<sup>139</sup> identified 4 groups of NPs containing Fe: homogeneously nucleated primary NPs of Fe; carbon agglomerates decorated with primary Fe NPs; agglomerates of Fe primary particles; and combined Fe/carbon agglomerates (Figure 4). Fe-bearing particles emitted from tailpipes often comprise a mixture of all these particle types.

Fe-bearing NPs in exhaust emissions might originate from several sources. Magnetite was found in exhaust emissions

when fuel additives (e.g., ferrocene) had been used (e.g., ref 140). Magnetic NPs may form due to Fe impurities in fuel which can convert to Fe oxides, such as magnetite and/or hematite, depending on combustion conditions.<sup>13,78,86,97</sup> Ferromagnetic NPs might also originate from aging of steel in the engine<sup>141</sup> and/or melting of engine fragments in the combustion chamber and subsequent crystallization during cooling.<sup>137</sup> In modern engines, however, various coatings (mainly Al, Cr, Mo, Ti, Zr alloy) reportedly reduce the wear rate by up to 94%.<sup>142</sup>

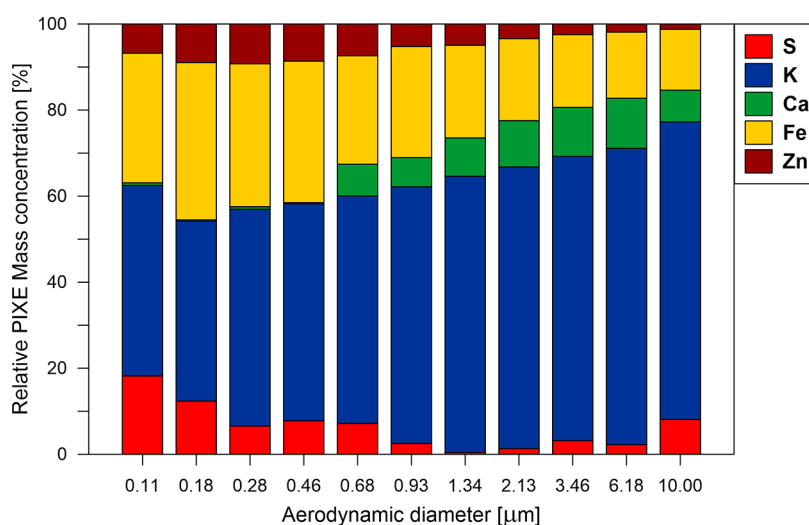
Studies on animals showed that exposure to exhaust emissions might be associated with developmental impairment in various ways, including changes in growth, sexual development, hormone levels, weight of the reproductive and accessory organs, expression of immune-related genes and susceptibility to allergies (e.g., refs 143–145). The exposure to diesel and biodiesel emissions might also lead to cardiovascular alterations as well as pulmonary and systemic inflammation in mice.<sup>146</sup> Gasoline-derived PM has also been associated with health problems, e.g., impairment of epithelial defense mechanisms.<sup>147</sup> Moreover, a study by Cheung et al.,<sup>148</sup> evaluating the oxidative potential of gasoline, diesel and biodiesel emissions, showed that soluble Fe is strongly associated ( $R = 0.99$ ) with particulate ROS activity (see Table SI 3, Supporting Information for more details).

### 4. BRAKE WEAR EMISSIONS

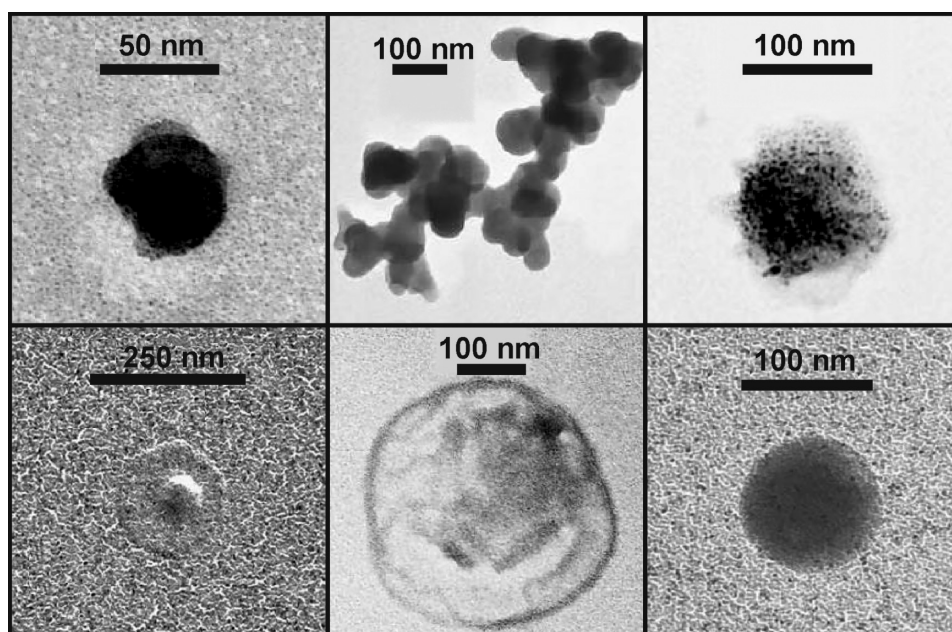
Brake wear debris comprises primarily carbonaceous and metal-bearing components.<sup>149</sup> In contrast to tailpipe emissions, Fe often dominates, constituting >50 wt % of all brake wear emissions.<sup>150–153</sup> Besides Fe, brake dust emissions can also contain a wide range of elements, including Cu, C, Ba, Sb, Si, Al, Mo, S, Sn, Cd, Cr, Pb, Zr, Ti and Zn.<sup>96,134,152,154–157</sup>

Table SI 4 (Supporting Information) shows total particle number and mass of nonvolatile brake dust emissions during a pin-on-disc test of a commercial, low-metallic brake pad.<sup>134</sup> The NP fraction (<100 nm) constitutes >90% of total particle number. Similarly, Garg et al.<sup>149</sup> reported that most particles were <30 nm (cf. Figure 3).

Although Fe-rich particles have been widely reported in brake wear studies,<sup>12,134,150,152,154,158</sup> little attention has yet been paid to identification of their properties (phase/mineralogical composition, concentrations of particular phases, size distribution) or potential health impact. Figure 5 shows an agglomerate of NPs 20–100 nm in size, derived from brake wear collected during a dynamometer test of a widely available



**Figure 6.** Relative mass concentration of Zn, Fe, Ca, K and S in tire wear, excluding dominating mineral elements Al and Si (adapted from Gustafsson et al.<sup>99</sup>).



**Figure 7.** TEM images of tire wear NP generated by a road simulator (adapted from Dahl et al.<sup>185</sup>). No compositional data were provided by the authors.

brake pad. These brake-wear NPs contain mostly magnetite and elemental Fe.<sup>154</sup> Other authors have reported other Fe oxides, mainly hematite, wüstite (FeO) and maghemite in the NP fraction.<sup>12,134,155</sup>

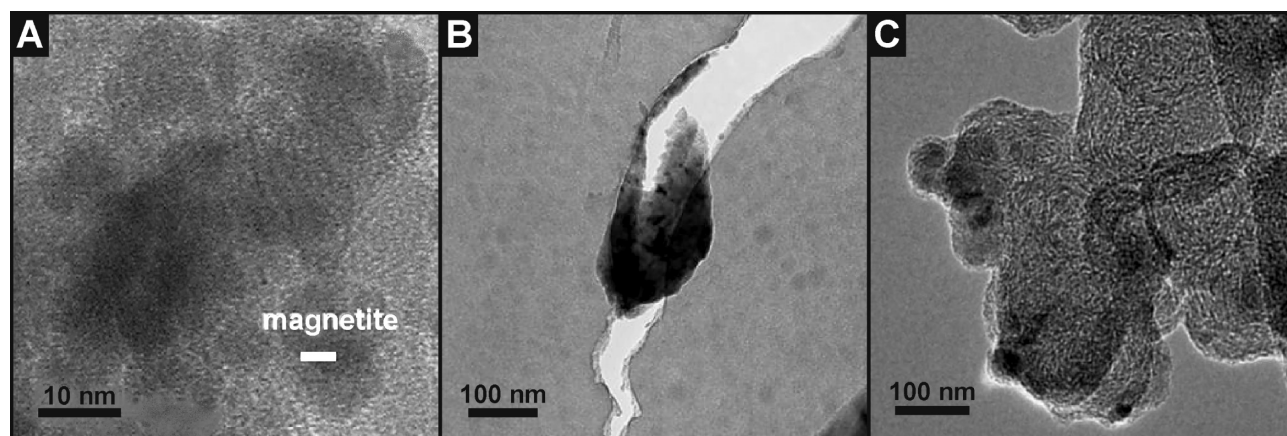
Brake wear debris results from friction between a brake pad, of diverse chemical compositions, and the cast iron brake disc. Both members of this friction couple can be a source of Fe-bearing NPs. Moreover, nano- and submicrometer-sized Fe powder, as magnetite, is often added (in concentrations up to 50 wt %) to brake pads,<sup>159</sup> as a solid lubricant. At brake pad temperatures below 200 °C, abrasive processes dominate, and wear particles >1 μm are mostly generated. But at higher temperatures (>190 °C), the concentration of nanosized grains (<100 nm) increases due to evaporation, condensation and aggregation processes.<sup>134,149,152,154</sup> As a result, high numbers (10<sup>11</sup> particles/stop/brake) of Fe-rich NPs are emitted.<sup>96,134,149,152,154,160,161</sup> The NP emission rate increases by

4–6 orders of magnitude at a critical temperature, usually 160 to 190 °C.<sup>162–165</sup>

*In vitro* and *in vivo* studies (see Table SI 3, Supporting Information) show that brake wear emissions can induce oxidative stress and chromosomal damage, invoke pro-inflammatory response and cause increased ROS production.<sup>166–173</sup> The effects were more severe for the emissions originating from nonasbestos organic brake pads, compared to low-metallic ones.<sup>171,174</sup>

Since NPs constitute the great majority of brake wear particle numbers, and Fe is the dominant component of those NPs, brake wear dust thus comprises a major source of airborne Fe-bearing NPs (see also Section 11).





**Figure 8.** TEM images of (A) magnetite NPs found in subway PM (adapted from Moreno et al.<sup>94</sup>) and (B) aircraft-derived NPs containing mainly Fe, Cr and Ni (adapted from Mazaheri et al.<sup>246</sup>), (C) ship-derived soot particles with V-, Fe- and Ni-bearing speckles of 5–10 nm (adapted from Streibel et al.<sup>247</sup>).

## 5. TIRE AND ROAD SURFACE WEAR EMISSIONS

Other types of traffic-related NPs, from tire and road surface wear, contain lower concentrations of Fe-bearing NPs, but still display high genotoxicity and potential hazard to human health.<sup>175–178</sup>

Tire wear debris typically comprises 47% rubber, 21.5% carbon black and as much as 16.5% metals.<sup>179</sup> Dominant components of tire wear include *n*-alkanes, *n*-alkanoic acids, PAHs, benzothiazoles<sup>110,120,151,157,178,180–184</sup> and elements such as Al, Si, Zn, Fe, S, K, Ca, Ti and Mg (Figure 6).<sup>99,157,176</sup> Notably, studies showed that Fe occurs in all size fractions <10  $\mu\text{m}$  of tire wear emissions, with concentrations up to 37 wt % in the fractions <460 nm (Figure 6).<sup>99</sup>

The PM (mass and number) emitted from tire/road surface wear depends on several factors, i.e., speed, slip angle, load and longitudinal force.<sup>99,135,185</sup> Tire/road surface wear particles >10  $\mu\text{m}$  constitute 60–70%, PM<sub>10</sub> 30% and PM<sub>2.5</sub> 4.5% of total tire emission mass.<sup>186</sup> However, tire wear accounts for a negligible portion (<5%) of road dust mass, contributing mainly to the NP (<100 nm) fraction<sup>135,185</sup> (cf. Figures 3 and 7), whereas road surface wear is responsible for emission of the larger grains.<sup>99,186</sup> Foitzik et al.<sup>135</sup> found that the PSD of tire NP emissions is bimodal (with peaks at 10 and 25 nm) or unimodal (peak at 10–15 nm) (cf. Figure 3). Other authors report number PSDs with slightly larger grains (main peak 25–45 nm).<sup>99,185,187</sup> Some authors, however, dispute NP generation during real-world conditions.<sup>188</sup>

The interaction between tires, road surface and traction sanding (sand introduced on the road surface to improve vehicle traction) results in emission of substantial particle numbers, especially in, for example, Nordic countries and Japan where studded tires are used regularly during winter.<sup>189</sup> NPs from tires might derive from the evaporation of semivolatile softening oils at temperatures >100 °C,<sup>185</sup> or inclusions of zinc oxides and sulfates.<sup>99,176,185</sup> Moreover, steel (and other metals) is often added (up to 25 wt %) as reinforcement material<sup>190</sup> so is likely to be an additional source of tire-derived Fe-bearing NPs.

Toxicological studies (see Table SI 3) suggest that tire/road surface wear poses a threat to human health via damage to epithelial cells and ROS formation.<sup>175–178</sup>

## 6. RESUSPENSION OF ROADSIDE DUST

Resuspension of road dust is one of the major sources (27–38 wt %) of airborne PM in urban environments (e.g., refs 109, 191–194). PM fractions >1  $\mu\text{m}$  are predominant in resuspended dust,<sup>75,109,186,195,196</sup> with submicrometer particles constituting ~10–15 wt %.<sup>186</sup>

High Fe concentrations (11,000–94,000 ppm) have been observed in the submicrometer fraction of roadside PM<sup>13</sup> in several different forms: magnetite, hematite, metallic Fe, ferrihydrite and goethite (Figure 2).<sup>13,197–204</sup>

Roadside dust can be a complex mixture of natural, soil-derived particles, and of traffic- (both exhaust and nonexhaust) and industry-derived emissions. Hence, exposure to resuspended dust may also be hazardous to human health.

## 7. UNDERGROUND, TRAIN AND TRAM EMISSIONS

Underground transport systems are used daily by approximately 4 million people in London,<sup>205</sup> 4.5 million in New York<sup>206</sup> and 7 million in Tokyo.<sup>207</sup> Although commuting typically constitutes only ~10% of the day (e.g., refs 208, 209), subway commuters are exposed to high levels of pollutants,<sup>210</sup> especially Fe-bearing NPs.<sup>94,211</sup> Daily average PM<sub>2.5</sub> levels in subway environments reach 480  $\mu\text{g}/\text{m}^3$  and particle number concentrations (PNC) up to 31,000 particles/cm<sup>3</sup>,<sup>94,212–214</sup> greatly (up to 30 times) exceeding nearby above-ground PM levels, e.g. in Helsinki,<sup>212</sup> Rome,<sup>215</sup> Seoul,<sup>216</sup> Buenos Aires,<sup>217</sup> Paris<sup>218</sup> or Mexico City.<sup>219</sup>

Fe is a dominant element in subway, train and tram emissions, in coarse (10–2.5  $\mu\text{m}$ ), fine (<2.5  $\mu\text{m}$ ) and NP (<100 nm) fractions,<sup>94,214,217,219–229</sup> constituting usually 65 wt % of PM<sub>10</sub> and PM<sub>2.5</sub> (e.g., refs 213, 225, 228), sometimes reaching levels as high as 86 wt % of PM<sub>10</sub>,<sup>221</sup> 88 wt % of PM<sub>2.5–1.0</sub><sup>211</sup> and 95% of PNC.<sup>211</sup> Fe is usually accompanied by other metals, including Cu, Ba, Zn, Si, Al, Ca, Ni, Ti, Sb, V, Co, Cr, Mn.<sup>94,214,225,230,231</sup>

The PSD of subway emissions is dominated by NPs <100 nm.<sup>220–222,232</sup> Airborne PM at subway stations contains a mixture of magnetite, maghemite and hematite, with some additional evidence of the presence of metallic Fe, wüstite and Fe oxyhydroxides (goethite and/or lepidocrocite).<sup>94,219,220,222,227,233–236</sup> Fe-bearing NPs of 5–50 nm usually occur in the form of spherical, agglomerated grains of metallic Fe with oxidized rims of magnetite and/or hematite

(Figure 8A).<sup>94,220,222,227,235</sup> Some studies identify hematite as the dominant Fe phase in subway airborne NPs;<sup>220,235</sup> others find magnetite in the highest concentrations.<sup>227,233</sup> It is evident that the composition of particulate air pollution is variable with location, and hence, that impacts on human health may also differ by location. The Fe oxidation level is important in terms of health hazard (see Section 12); thus more data are needed to quantify the magnetite/hematite contributions to total subway PM and if necessary, to identify and introduce mitigation measures limiting subway PM emissions.<sup>237,238</sup>

Subway-derived Fe-bearing NPs may form from braking,<sup>94,211,230,231</sup> wheel/rail track interactions<sup>232,235,239</sup> or sparking between a third-rail and collectors.<sup>220</sup> The presence of coexisting metallic Fe (often with oxidized rim), magnetite, maghemite and hematite suggests that particular Fe oxides reflect increasing stages of oxidation.<sup>94</sup>

Fe-rich subway particles have been found to be toxic (see Table SI 3, Supporting Information), causing mitochondrial depolarization, inflammatory responses and generation of ROS,<sup>229,233,240–245</sup> especially in the case of fractions <2.5  $\mu\text{m}$  and <0.18  $\mu\text{m}$ .<sup>244</sup> Karlsson et al.<sup>233</sup> found that subway particles are 8 times more genotoxic than roadside PM collected nearby a very busy street. The high genotoxicity of subway-derived PM probably results from synergistic effects of Fe-, Cu- and Zn-bearing, subway-derived pollution, possibly in the fraction <0.1  $\mu\text{m}$ .<sup>241,244</sup>

Trams and trains generate similar Fe-bearing NPs (e.g., refs 76, 223, 224, 248), which may be particularly hazardous at subway stations and/or tunnels due to confined spaces, poor ventilation and high congestion. Hence, commuters using underground systems are exposed to high levels of metal-rich, potentially hazardous airborne particulates.<sup>210</sup>

## 8. AIRCRAFT EMISSIONS

Masiol and Harrison<sup>249</sup> have reviewed aircraft emissions and other airport-related contributions to ambient air pollution. Airports, and their associated road traffic, are a source of Fe-bearing NPs.

Nanoparticulate aircraft emissions are dominated by soot particles, accompanied by smaller amounts (4–6 wt %) of Fe,<sup>100,246,250–253</sup> and other metals, including Cr, Ni, Ca and K.<sup>246,250</sup>

Number-normalized PSDs of aircraft emissions are dominated by NPs (<100 nm), with a main peak at 10–20 nm.<sup>246,254–259</sup>

From TEM and EDX, aircraft-derived Fe-bearing NPs occur in the form of magnetite and/or maghemite (Figure 8B).<sup>100</sup> The presence of Fe in soot agglomerates might arise from chemical/mechanical corrosion of the liquid fuel atomizer.<sup>100</sup> Fe-bearing NPs in aircraft emissions might also originate from impurities in the kerosene fuel.<sup>251</sup>

Aircraft emissions are reported to have deleterious health impacts both globally and locally.<sup>260,261</sup> Aircraft-generated NPs, at Santa Monica Airport, Southern California, USA, occurred at concentrations 11, 10, 5 and 2.5 times the background value for sites at distances from the airport of 80, 100, 380 and 660 m, respectively.<sup>256</sup> Enhanced, aircraft-derived levels of NPs (up to 20 $\times$  background concentrations) persisted up to 900 m from a takeoff area,<sup>255–257</sup> thus likely exerting an adverse influence on adjacent neighborhoods (see Table SI 3, Supporting Information). Furthermore, there have recently been several lawsuits related to “aerotoxic syndrome”, linked to occupational exposure to polluted cabin air and associated with

severe headaches, mental confusion, sight problems, insomnia, digestive and respiratory problems, and even death.<sup>262</sup> The impacts of aircraft emissions on human health are poorly understood, but some evidence indicates that occupational exposure of airport personnel and aircraft crew has detrimental effects.<sup>249,262–266</sup>

## 9. SHIPPING EMISSIONS

Shipping emissions, derived from combustion of so-called “bunker fuel”, affect air quality both locally<sup>267–271</sup> and globally.<sup>272–274</sup>

Most studies to date have focused on NO<sub>x</sub>, SO<sub>2</sub>, CO and CO<sub>2</sub> as they constitute the majority of ship-derived emissions.<sup>267,273,275–279</sup> Fe-bearing particles occur in the PM<sub>2.5</sub> fraction in concentrations up to 10  $\mu\text{g}/\text{m}^3$ ,<sup>91,247,270,280–286</sup> usually accompanied by other metals, including V, Ni, Zn, Ca, Na, P.<sup>91,282–284,286</sup> Using cluster analysis of elemental composition and electron microscopy observations, Popovicheva et al.<sup>284</sup> distinguished 5 groups of particles in shipping emissions. The Fe-rich group, constituting 3–4% of all PM mass, comprised 50% Fe, with smaller portions of Si, S and Ca.

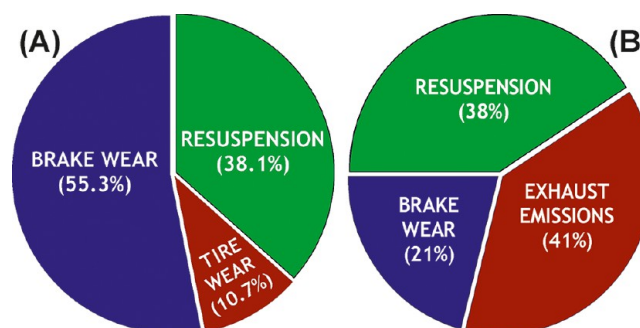
Shipping-derived Fe-bearing particles occur usually in the fraction <100 nm, in the form of 5–10 nm inclusions in soot particles (Figure 8C).<sup>247,285</sup> The NPs have been observed in the forms of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>S, Ni<sub>2</sub>Fe, Ni<sub>3</sub>Fe, Ni<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub>.<sup>91,284</sup>

Those inclusions are formed as a result of the decomposition or oxidation of Fe-bearing minerals in heavy fuel oil, and/or corrosion of the engine.<sup>284</sup>

Exposure to shipping-derived particles (see Table SI 3, Supporting Information) results in acute cytotoxic effects in cell cultures *in vitro*<sup>286,287</sup> and oxidative stress.<sup>288</sup> Shipping emissions are related to 60,000 cardiopulmonary and lung cancer deaths annually.<sup>289</sup> In busy ports, the health impacts of shipping-derived Fe-bearing NPs are additive to the NP loadings from associated road/freight traffic.

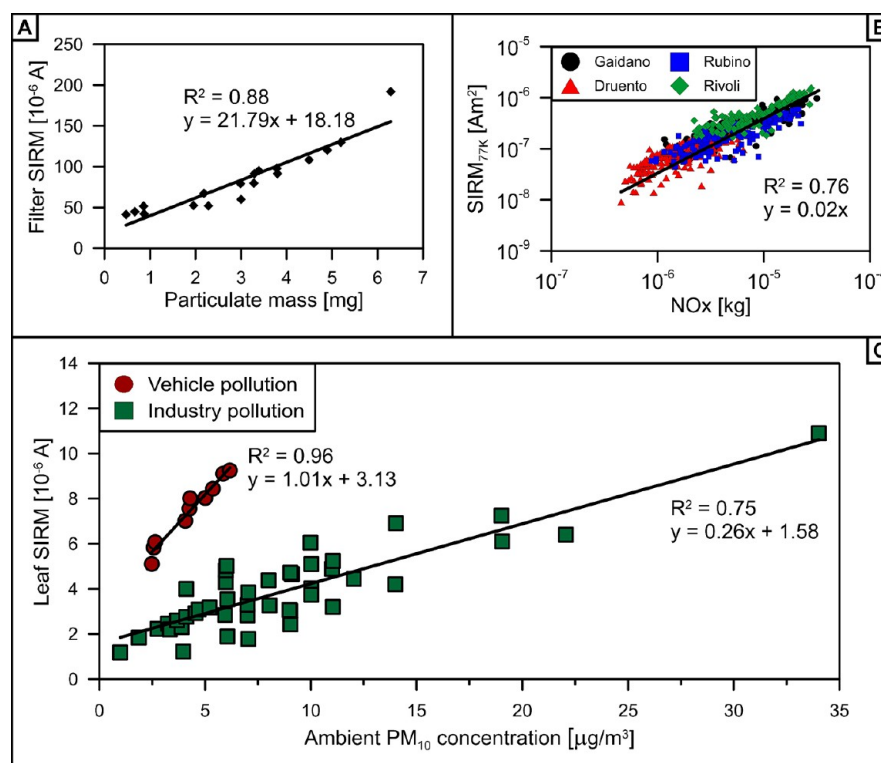
## 10. SOURCE APPORTIONMENT OF ROADSIDE-DERIVED PM

Estimation of the contributions made by specific sources to total airborne PM or PNC is often difficult, and variable between different studies (Figure 9).<sup>191,194,290–295</sup> For a street canyon in Zurich, and using elemental data and positive matrix factorization (PMF) to distinguish between sources, Bukowiecki et al.<sup>191</sup> found that brake wear, exhaust emissions and



**Figure 9.** Source apportionment of (A) nonexhaust PM emissions (adapted from Harrison et al.<sup>292</sup>) and (B) total traffic-derived PM (adapted from Bukowiecki et al.<sup>191</sup>).





**Figure 10.** Correlation between: (A) air filter SIRM and roadside PM<sub>10</sub> mass in Lancaster, UK (adapted from Mitchell and Maher<sup>79</sup>); (B) air filter SIRM at 77K (SIRM<sub>77K</sub>) and concentration of total nitrogen oxides (NO<sub>x</sub>) at the roadside, in Turin, Italy (adapted from Saragnese et al.<sup>315</sup>); (C) leaf SIRM and ambient PM<sub>10</sub> concentrations, derived from vehicle pollution and industrial stack point source pollution (adapted from Mitchell et al.<sup>322</sup> and Hansard et al.<sup>80</sup>).

resuspension contributed 21%, 41% and 38% of total traffic-derived PM<sub>10</sub> mass, respectively (Figure 9B). Lawrence et al.<sup>194</sup> studied PM in a tunnel in Hatfield, UK, relying on principal component analysis (PCA) and multiple linear regression analysis, and reported that resuspension was responsible for 27% of PM<sub>10</sub> mass, diesel emissions for 21%, gasoline emissions for 12%, brake wear for 11%, road surface wear for 11%, with 18% of PM<sub>10</sub> mass not attributed to any source. Harrison et al.<sup>292</sup> studied roadside PM at a busy London street, assessing the contribution of nonexhaust emission sources using specific elemental tracers, i.e., Ba for brake emissions and Zn for tire emissions. They found that the mass of brake wear (0.9–11.5  $\mu\text{m}$ ) was higher than that of resuspended dust ( $55.3 \pm 7.0\%$  versus  $38.1 \pm 9.7\%$  of nonexhaust emissions). In this study,  $10.7 \pm 2.3\%$  of nonexhaust PM (0.9–11.5  $\mu\text{m}$ ) was attributed to tire wear (Figure 9A).

Some source apportionment studies have considered particle number and volume of PM<sub>10</sub> (e.g., refs 291, 293). The authors found that exhaust emissions accounted for 22.4% of total volume and 65.4% of total number, brake dust 13.7% of total volume and 1.7% of total number, and resuspension 4.4% of total volume and 4.8% of total number. Tire wear emissions were not identified in this study.<sup>291</sup>

Discrepancies between these estimates probably reflect the differing methodologies, instruments and characteristics of the sampling sites. There is presently no unambiguous tracer of resuspended dust, which makes estimation of the resuspension contribution challenging.<sup>109</sup> Pant and Harrison<sup>109</sup> provide a detailed description of methodologies for the assessment of source apportionment of urban PM.

Around the world, there are numerous emission standards limiting exhaust emissions, e.g., European Emission Standard (EURO) in European Union (EU), Tier motor vehicle emission and fuel standards in USA, WLTC-based (Worldwide Harmonized Light Vehicles Test Cycle) regulation in Japan, or Bharat Stage regulation in India.<sup>296</sup> In response to increasing regulation, the automotive industry has sought, with varying measures and outcomes, to reduce exhaust emissions. Non-tailpipe emissions are currently unregulated; yet constitute a similar proportion of total mass traffic-derived PM as exhaust emissions (Figure 9B).<sup>191,297,298</sup> Resuspension may become a more substantial source of roadside PM, as electrification (both electric engines and regenerative braking systems) of the vehicle fleet will decrease both exhaust and brake wear emissions.<sup>299</sup> Further research is needed to quantify the resuspension contribution to roadside PM.

## 11. MAGNETIC MEASUREMENTS OF VEHICLE-DERIVED, IRON-BEARING NANOPARTICLES

The majority of the Fe-bearing particles emitted by vehicles occur as ferromagnetic (*sensu lato*), i.e., magnetically ordered, minerals, especially as magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and metallic  $\alpha\text{-Fe}$ .<sup>12,76–80,87,92,300</sup> Thus, magnetic analyses, based on concentration- and magnetic grain size-dependent parameters, enable characterization and quantification of vehicle-derived PM (e.g., refs 76, 79, 300–302).

Magnetic methods have enabled mapping of heavy metal contaminations in soils (e.g., refs 303–305), as well as PM concentrations in the urban atmosphere (e.g., refs 80, 92, 248,

306–308). Hofman et al.<sup>309</sup> review data from biomagnetic monitoring studies of air pollution (see also Table SI 6, Supporting Information).

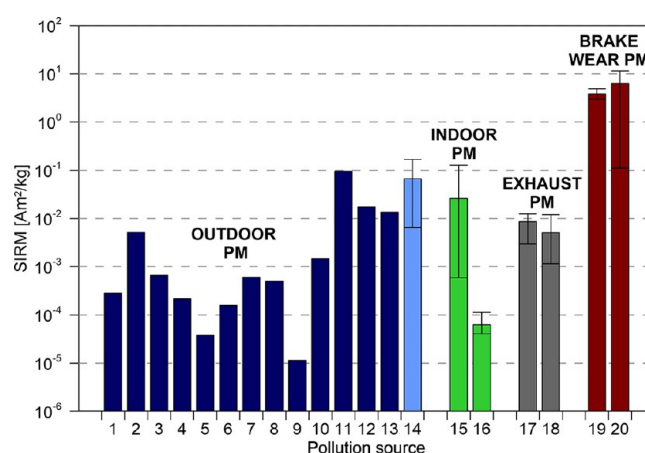
Significant correlation has frequently been found between  $PM_{10}$ ,  $NO_x$ , heavy metal content and concentration-dependent magnetic properties (e.g., magnetic susceptibility, saturation isothermal remanent magnetization) of PM (Figure 10).<sup>78–80,248,300–302,310</sup> The magnetite content of roadside  $PM_{10}$  appears greater than  $PM_{10}$  from a power generation emissions stack (Figure 10c).<sup>80</sup> An early study identified strong correlation ( $n = 55$ ;  $R^2 = 0.79$ ) between magnetic susceptibility of airborne PM and mutagenicity.<sup>311</sup> Moreover, other composition- and magnetic grain size-dependent magnetic parameters (e.g., hysteresis properties, first-order reversal curves) have often been helpful in the distinction between different sources of vehicle-derived pollutants (e.g., refs 312–314). For example, Sagnotti et al.<sup>312</sup> and Sagnotti and Winkler<sup>314</sup> showed that exhaust emissions have distinctive magnetic hysteresis properties compared to brake wear emissions.

Magnetic NPs <30 nm in size display a distinctive magnetic behavior; they are “superparamagnetic” (SP), unable to hold a magnetic remanence at room temperature, due to thermal agitation of their magnetic moments. Several magnetic studies have reported on the ultrafine, SP fraction of airborne roadside pollution.<sup>76,300,312–317</sup> In Munich, Germany, SP ferrites contributed 22% to the total saturation isothermal remanent magnetization (SIRM) of roadside PM and the SP fraction was dominated by 10–16 nm grains of maghemite and 5–8 nm grains of  $\alpha$ -Fe.<sup>76</sup> Higher SP contributions to the SIRM of roadside PM, even up to 88%, have since been reported,<sup>312,315</sup> possibly reflecting different measurement temperatures. Muxworthy et al.<sup>76</sup> measured SIRM at 77 K, Sagnotti et al.<sup>312</sup> at 4 K and Saragnese et al.<sup>315</sup> at 15 K. Due to thermal agitation, grains of magnetite <16 nm, maghemite <22 nm and hematite <11 nm are unable to retain magnetic remanence at 77 K<sup>318–321</sup> and therefore are magnetically “invisible” at this temperature. It should be noted that the SP fraction might occur not only as discrete magnetic grains <30 nm in size but also as oxidized rims around larger particles.<sup>319</sup>

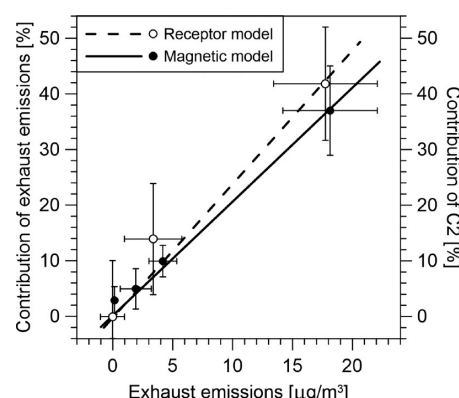
Magnetic PM, containing redox-active Fe, might not only be harmful to human health on its own; it is also usually associated with other toxic components, including Ba, Br, Cr, Cu, Mn, Mo, Ni, Pb, Zn<sup>10,13,75,302,323</sup> and PAHs.<sup>310,324</sup>

Critically, although Fe-bearing fine (<2.5  $\mu m$ ) and nanosized (<0.1  $\mu m$ ) particles are present in almost all types of traffic-derived emissions (see previous sections), the magnetic signatures of specific particle sources appear to be distinctive (Figure 11; see also Table SI 5, Supporting Information). For example, the ferrimagnetic content of brake wear PM greatly exceeds that of many other PM sources (Figure 11). Furthermore, the SP fraction of brake wear emissions contributes 35% of SIRM, compared to 20% SP contribution in gasoline tailpipe emissions.<sup>313,314</sup> Component analysis of magnetic coercivity distributions of roadside  $PM_{10}$  in Switzerland enabled identification of two magnetic components/PM sources: the first (C1), resuspended dust (a mixture of natural and anthropogenic street dust); the second (C2), traffic exhaust emissions (Figure 12).<sup>302</sup>

Conventional, elemental analysis of Fe, which is present in high concentrations at urban roadsides (see previous sections) cannot differentiate between its different vehicular sources. In contrast, magnetic methods of PM analysis can distinguish



**Figure 11.** Saturation magnetic remanence (SIRM) for indoor and outdoor PM (adapted from Halsall et al.<sup>77</sup> and Hansard et al.<sup>92</sup>), exhaust and brake wear emissions:<sup>325</sup> 1, wood fired boiler; 2, coal fired boiler; 3, gas/oil boiler; 4, oil fired boiler; 5, gas kettle incinerator; 6, coal fired power station; 7, gas/oil power station; 8, graphite plant; 9, smelting plant; 10, coke; 11, sinter; 12, BOS slag; 13, iron ore pellets; 14, roadside filters from Halsall et al.;<sup>77</sup> 15, indoor filters from Halsall et al.;<sup>77</sup> 16, printer dust from Gonet et al.;<sup>325</sup> 17, diesel emissions from Gonet et al.;<sup>325</sup> 18, gasoline emissions from Gonet et al.;<sup>325</sup> 19, airborne brake wear emissions, from Gonet et al.;<sup>326</sup> and 20, nonairborne brake emissions, from Gonet et al.<sup>326</sup>



**Figure 12.** Absolute and relative contributions of exhaust emissions to  $PM_{10}$  at several sites in Switzerland. Open circles and dashed best-fit line refer to the receptor model (chemically estimated  $PM_{10}$  mass contribution of exhaust emissions). Solid dots and the solid best-fit line refer to the magnetic model, where component C2 (identified using magnetic component analysis) corresponded to exhaust emissions (adapted from Spassov et al.<sup>302</sup>).

between different Fe minerals and oxidation states ( $Fe^{2+}$  vs  $Fe^{3+}$ ), information on particular potential value regarding Fe-bearing NP toxicity and human health impacts (see Section 12). Moreover, given distinctive magnetic fingerprints from different PM sources, combining elemental and magnetic analyses may enable more accurate and precise source apportionment (cf. Figure 12).

## 12. SPECIFIC TOXICITY OF IRON-BEARING NANOPARTICLES

Exposure to airborne Fe-bearing NPs may be particularly hazardous to human health due to their high bioreactivity and potential toxicity, combined with their abundance in the urban environment. Numerous studies have shown that Fe plays an

important role in the generation and pathogenicity of ROS.<sup>3,327–335</sup> Dusseldorp et al.<sup>328</sup> found that airborne Fe was associated with exacerbation of some respiratory symptoms. Fe-rich particles have been shown to generate ROS and provoke an inflammatory response.<sup>331</sup> These findings are supported by the results obtained by Pelclova et al.<sup>334</sup> who found elevated oxidative stress markers in exhaled breath condensate of workers exposed to NPs during Fe oxide pigment production (see also Table SI 3, Supporting Information).

The presence in the human brain specifically of magnetite, a strongly magnetic, mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> oxide, is important because it has been causally linked with neurodegenerative diseases. Magnetite in brain tissue has been observed to be directly associated with AD plaques (e.g., refs 336–338) and correlated (albeit with rather small sample size) with the incidence of AD.<sup>339,340</sup> Neuropathological changes associated with AD include the formation of senile plaques, containing amyloid- $\beta$  fibrils. When associated with redox-active transition metal ions, such as the Fe<sup>2+</sup> ions contained within magnetite, amyloid- $\beta$  can generate damaging ROS, directly contributing to oxidative brain damage, a key early feature of AD (e.g., refs 74, 341, 342). *In vitro* experimental data additionally show that magnetite acts synergistically to enhance the toxicity of amyloid- $\beta$ .<sup>341,343</sup> Moreover, higher concentrations of magnetite have been also detected in brain tumor tissue, in meningioma<sup>344,345</sup> and in diseased hippocampal tissues,<sup>346</sup> compared to healthy brain tissue.

*In vitro* studies on A549 human epithelial cells have shown that exposure to magnetite (Fe<sub>3</sub>O<sub>4</sub>) leads to acute cytotoxic effects and generation of ROS.<sup>347</sup> In the case of the NP fraction (<0.1  $\mu$ m), the health response (DNA damage) was more severe than with larger particles (0.2–10  $\mu$ m).<sup>348</sup> Assessment of the “theranostic” use of SP iron oxide nanoparticles (SPIONs) has also shown that exposure to these particles can lead to toxic effects, including DNA damage, ROS generation, chromosome condensation, formation of apoptotic bodies, inflammation, impaired mitochondrial function and membrane leakage of lactate dehydrogenase (e.g., refs 349–352; see also Table SI 3, Supporting Information).

Fe<sup>2+</sup> is toxic as it may cause the generation of ROS via the Fenton reaction:<sup>68</sup>



The hydroxyl radical (HO $\cdot$ ) is especially dangerous in brain tissue as it might cause oxidative stress, which is a hallmark of neurodegenerative diseases like AD (e.g., refs 74, 341, 342). Until recently, the magnetite particles found in the human brain were assumed to be entirely of *in situ*, biogenic origin.<sup>353,354</sup> It has been suggested that the normal processes for safe storage (within ferritin cores) and transport of the brain Fe become dysfunctional as a result of neurodegeneration (e.g., ref 74). However, Maher et al.<sup>10</sup> identified, for the first time, the abundant presence in the human brain of externally derived, magnetite pollution NPs. These magnetite NPs displayed a range of particles sizes (from 10 to 150 nm), were frequently rounded or even spherical, and often associated with other “exotic” transition metal NPs, containing Pt, Ni, Co and Cu. Some have fused surface crystallites that would be very difficult to reconcile with *in situ*, low temperature growth or dissolution formation processes.

Thus, airborne magnetic pollution NPs may pose a threat to human health due to their bioreactivity, their ability to penetrate every organ, including the brain, their link with neurodegenerative diseases and their abundance in the urban atmosphere.

### 13. PERSPECTIVES AND OUTLOOK

Many studies have identified adverse health effects associated with exposure to particulate air pollution (e.g., refs 28, 355). Traffic-derived emissions are a major source of urban PM, constituting up to 80% of airborne concentrations of PM in the urban environment.<sup>109</sup> Hence, improved understanding of the biological interactions induced in the human body by traffic-derived PM is of critical importance for identifying their specific pathways of impact, and relative priority in terms of their abatement and/or mitigation.

Metal-bearing NPs may be especially hazardous to human health. Studies on mouse models and human epithelial cells have demonstrated the detrimental impact of NPs (e.g., refs 20, 356), with Fe-bearing NPs of particular potential hazard (e.g., refs 3, 330). Combustion- and friction heating-derived, Fe-bearing NPs found in human brain<sup>10</sup> are especially worrisome, due to the high redox activity of magnetite and its potential association with neurodegenerative diseases, such as Alzheimer’s or Parkinson’s diseases.<sup>10,68,338</sup> Given the abundant occurrence of Fe-bearing NPs in the environment (indoor and outdoor), workplace, and in biomedical applications, and the inconsistency of the data reporting their effects on biological systems, more systematic studies on nanosized, Fe-bearing particles are needed in order to define their toxic potential.

Traffic-related air pollution has been shown to be associated with respiratory, cardiovascular and neurological problems (e.g., refs 28, 357). However, little is known about long-term health effects of ambient NPs. Recently, studies have examined regression models of health outcomes and the spatial distribution of NPs (e.g., refs 358–363). These models can be useful in the assessment of chronic health effects of NPs using population-based cohorts. Ostro et al.<sup>364</sup> observed statistically significant associations between ischemic heart disease (IHD) mortality and both PM<sub>2.5</sub> and PM<sub>0.1</sub> fractions. Moreover, some specific components were observed to be independently associated with IHD mortality, including gasoline/diesel emissions and metals (Fe and Cu).<sup>364</sup> The results of Weichenthal et al.<sup>361</sup> suggest that exposure to ambient NPs is directly associated with the incidence of prostate cancer. Bai et al.<sup>365</sup> found that chronic exposure to NPs may increase the incidence of hypertension and diabetes. Land use regression models can potentially be used, along with actual NP concentration measurements, as a basis for an assessment of human chronic exposures to NPs. Interestingly, Weichenthal et al.<sup>362</sup> did not observe evidence of positive associations between modeled long-term NP exposure and the incidence of respiratory disease.

It is worth emphasizing that humans are variably exposed not to a single, individual traffic-related source of particulates, but to a complex mixture of them. Some of the deleterious effects of particular particles/compounds can be accelerated by the presence of others. For example, adverse effects (for instance, lipid peroxidation in brain tissue) of Fe-bearing particles (for instance, from brake wear) are promoted by the presence of Al (for instance, from tire wear or natural, soil dust).<sup>366</sup> Although increasing numbers of epidemiological



studies have identified associations between exposure to traffic-derived air pollution and detrimental health impacts, the specific mechanisms of these associations remain imperfectly understood.

Furthermore, PM composition is variable not only from city to city but also within cities, such that different populations are exposed to different pollution mixes. Hence, the impacts of exposure to PM on human health likely also differ by location.

Exhaust emissions have been legally regulated for over 25 years (e.g., in EU since 1992, in USA since 1994, in India since 1991).<sup>296</sup> Initially, only the mass of CO (carbon monoxide), HC (hydrocarbons; in USA), NO<sub>x</sub> (nitrogen oxides; in EU and USA), PM (in EU and USA) and NMHC (nonmethane hydrocarbons; in USA) was limited. Subsequently, more parameters have been covered by these regulations, e.g., mass of VOC (volatile organic compounds) and PN (particle number).<sup>296</sup> It seems highly probable that legal regulation concerning brake wear emissions will be introduced in the near future, especially given their increasing importance as exhaust emissions decline with electrification of vehicle fleets. Given the growing evidence that Fe-bearing NPs may constitute a particular hazard to human health, regulation to limit these Fe-rich, strongly magnetic emissions may also become important and urgent, on an international scale.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.9b01505](https://doi.org/10.1021/acs.est.9b01505).

Search strategy; nonvehicle sources of Fe-bearing nanoparticles in the urban environment; summary table of selected toxicological studies of vehicle-derived PM; total particle number and mass of brake dust emissions during a dynamometer test; selected magnetic parameters of exhaust and brake wear emissions; inventory table of reported magnetic studies on pumped-air filters and tree leaves (PDF)

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### Notes

The authors declare no competing financial interest.

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