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Title: Spatial variation in ultrafine, vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves.

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Keywords: vehicle pollution, magnetism, lead pollution, roadside biomonitoring.

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Abstract: Exposure to metal-rich particulate pollution is associated with adverse health outcomes. In particular, lead has recently been shown to be toxic in young children even at low levels previously considered 'safe' (e.g. Koller et al., 2004). Lead poisoning from vehicle pollution has been addressed internationally by removal of leaded petrol but toxic blood lead levels in children continue to be reported in urban areas (Rabito et al., 2004; Mathee et al., 2002), the source possibly resuspended roadside soil, enriched in lead due to previous leaded fuel usage (Young et al., 2002; Filipelli et al., 2005). Here, we use paired geochemical and magnetic analyses of natural biomonitors - kerbside tree leaves -, and of air sample filters, to examine contemporary sources of particulate pollution, and show that co-associated, ultrafine (< 1 μ m) lead- and iron-rich particles are emitted as vehicle-derived pollutants. Higher and strongly correlated lead, iron and magnetic remanence values were found closer to roads and on the road-proximal rather than road-distal sides of trees. Critically, highest pollutant values occurred on tree leaves next to uphill rather than downhill road lanes. The lead content of the leaf particulates was associated only with sub-micrometre, combustion-derived spherical particles. These results indicate that vehicle exhaust emissions, rather than resuspended soil dust, or tyre, brake or other vehicle wear, are the major source of the lead, iron and

magnetic loadings on roadside tree leaves. Analysis of leaves at different heights showed that leaf particulate lead and iron concentrations are highest at ~ 0.3 m (i.e. small child height) and at 1.5 - 2 m (adult head height) above ground level; monitoring station collectors placed at 3 m height thus significantly underestimate kerbside, near-surface lead concentrations. These results indicate that vulnerable groups, especially young children, continue to be exposed to ultrafine, lead- and iron-rich, vehicle-derived particulates.

CENTRE FOR ENVIRONMENTAL MAGNETISM AND
PALAEOMAGNETISM

LANCASTER ENVIRONMENT CENTRE

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21.6.2007

Dear Peter

I write to submit a topical, interdisciplinary paper for consideration for publication in Atmospheric Environment, 'Spatial variation in ultrafine, vehicle-derived metal pollution identified by magnetic and elemental analysis of roadside tree leaves', by Maher, Moore and Matzka.

The submission consists of the text in one file, comprising ~ 6000 words (abstract 299 words), and 5 separate figures (eps format).

Please don't hesitate to get back to me with any queries. I hope you and yours are thriving and contented.

Best wishes

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1 Spatial variation in ultrafine, vehicle-derived metal pollution identified by magnetic
2 and elemental analysis of roadside tree leaves.

3

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11

12 Abstract

13 Exposure to metal-rich particulate pollution is associated with adverse health

14 outcomes. In particular, lead has recently been shown to be toxic in young children

15 even at low levels previously considered ‘safe’ (e.g. Koller et al., 2004). Lead

16 poisoning from vehicle pollution has been addressed internationally by removal of

17 leaded petrol but toxic blood lead levels in children continue to be reported in urban

18 areas (Rabito et al., 2004; Mathee et al., 2002), the source possibly resuspended

19 roadside soil, enriched in lead due to previous leaded fuel usage (Young et al., 2002;

20 Filipelli et al., 2005). Here, we use paired geochemical and magnetic analyses of

21 natural biomonitors - kerbside tree leaves -, and of air sample filters, to examine

22 contemporary sources of particulate pollution, and show that co-associated, ultrafine

23 (< 1µm) lead- and iron-rich particles are emitted as vehicle-derived pollutants.

24 Higher and strongly correlated lead, iron and magnetic remanence values were found

25 closer to roads and on the road-proximal rather than road-distal sides of trees.

26 Critically, highest pollutant values occurred on tree leaves next to uphill rather than
27 downhill road lanes. The lead content of the leaf particulates was associated only with
28 sub-micrometre, combustion-derived spherical particles. These results indicate that
29 vehicle exhaust emissions, rather than resuspended soil dust, or tyre, brake or other
30 vehicle wear, are the major source of the lead, iron and magnetic loadings on roadside
31 tree leaves. Analysis of leaves at different heights showed that leaf particulate lead
32 and iron concentrations are highest at ~ 0.3 m (i.e. small child height) and at 1.5 – 2 m
33 (adult head height) above ground level; monitoring station collectors placed at 3 m
34 height thus significantly under-estimate kerbside, near-surface lead concentrations.
35 These results indicate that vulnerable groups, especially young children, continue to
36 be exposed to ultrafine, lead- and iron-rich, vehicle-derived particulates.
37 Keywords: vehicle pollution, magnetism, lead pollution, roadside biomonitoring.

38

39 1. Introduction.

40 Particulate air pollutants have been found to be strongly associated with
41 adverse effects on respiratory health (e.g. Knox, 2006; Knutsen et al. 2004, Schwartz,
42 1996; Pope et al., 2002). The degree of hazard depends principally on the site of
43 particulate deposition within the lungs, in turn reflecting the size, shape and density of
44 the particulates, and their effects on biological tissue, determined by the composition
45 of the particles. Ultrafine particles ($< 2.5 \mu\text{m}$, $\text{PM}_{2.5}$) can be deposited deep within the
46 pulmonary region of the human respiratory tract when inhaled, with potential
47 bioavailability maximised by the large number and surface area of such particles. If
48 these particulates reach the alveoli, inflammation and diminished pulmonary function
49 can be incurred (e.g. Knutsen et al., 2004; Seaton et al., 1995). Links with lung
50 cancer (Pope et al., 2002; Beeson et al., 1998) and increased cardiovascular mortality

51 rates (Pope et al., 1995; Schwartz et al., 1996) have also been established. Large
52 proportions of such ultrafine particles are known to be emitted by vehicles (e.g.
53 Maricq, 1999), with diesel-powered vehicles producing several orders of magnitude
54 more PM_{2.5} particles than petrol-driven ones (Rudell et al., 1999; Maricq, 1999; Wang
55 et al., 2003). In terms of composition, analysis of urban anthropogenic particulates has
56 shown them to be enriched in a range of potentially toxic trace metals, including Fe,
57 Pb, Zn, Ba, Mn, Cd and Cr (Huhn et al., 1995; Harrison & Jones, 1995). Keyser et al.
58 (1978) reported that Pb and Cr from vehicle exhausts are preferentially associated
59 with particle surfaces, possibly as a result of condensation from the vapour phase or
60 adsorption from solution. Urban anthropogenic particulates also contain, almost
61 invariably, magnetic particles (e.g. Hunt et al., 1984; Flanders, 1994; Morris et al.,
62 1995; Matzka & Maher, 1999; Petrovsky & Ellwood, 1999). These derive from the
63 presence of iron impurities in fuels, which form upon combustion a non-volatile
64 residue, often a mix of strongly magnetic (magnetite-like) and weakly magnetic
65 (haematite-like) iron oxides. Magnetite has been identified specifically as a
66 combustion-derived component of vehicle exhaust materials (Abdul-Razzaq &
67 Gautam, 2001).

68 Quantitatively, the health risks of urban metal particulates are poorly
69 understood, due to a combination of confounding factors and the relatively low spatial
70 resolution of the data available for pollutant exposure. However, Pb is a significant
71 neurotoxin, posing some health risk even at levels previously considered safe,
72 particularly with regard to brain and kidney damage, hearing impairment and
73 diminished cognitive development in children (Koller et al., 2004; Lanphear et al.,
74 2000; Needleman & Landrigan, 2004). High levels of many other trace metals are
75 implicated in lung disease and central nervous system disorders (e.g. Colls, 2002),

76 ranging from learning disorders to dementia and possibly even Alzheimers's disease
77 (Calderón-Garcidueñas et al., 2004). Aggressive removal of lead from environmental
78 sources, especially petrol and paints, has resulted in major reductions in lead
79 poisoning of children. However, many urban areas still exhibit damagingly high
80 blood lead levels (i.e. > 5µg/dl) in children (e.g. Koller et al., 2004; Lanphear et al.,
81 2000; Mathee et al. 2002). In a study in the Indianapolis area, resuspended soil dust,
82 enriched with lead from previous decades of leaded fuel usage, was the suspected
83 major source, in light of higher blood lead levels at the urban roadside and seasonal
84 peaks (summer and winter) in blood lead (Filippelli et al., 2005).

85 Magnetic biomonitoring (Matka & Maher, 1999) may provide a robust and
86 cost-effective means both to gain significantly enhanced spatial resolution for
87 pollutant data, and test proposed metal source/health linkages. The deposition of
88 pollution particles on tree leaf surfaces has been shown to result in easily measurable
89 magnetic properties, including magnetic remanence (i.e. the magnetization remaining
90 after a sample has been placed in and then removed from an applied dc field) and
91 magnetic susceptibility (the magnetization induced when the sample is placed in a
92 small - ~ twice the Earth's magnetic field – dc field). Leaves are potentially efficient
93 receptors and biomonitors of particulate pollution, as they provide a large total surface
94 for particle collection, numbers of samples and sample sites can be high (i.e. 100s),
95 and, in pollution contexts, the leaves themselves are insignificantly magnetic. Tree
96 leaves also preclude sampling problems associated with use of artificial particle
97 collectors (including power requirements, noise, and vulnerability to vandalism). To
98 ensure comparability of results, tree leaves of the same tree species, and similar age,
99 can be used. For a number of industrial sites in N. Germany, Schadlich et al. (1995)
100 found strong correlation between the magnetic susceptibility of pine needles and their

101 Fe content, as a result of deposition of fly ash particles. For a relatively small city
102 with little industry (Norwich, U.K.; population ~100,000), Matzka & Maher (1999)
103 found minimal values of magnetic remanence for birch leaves in parks within the city
104 centre but increasingly high values for trees located at the roadside, and significantly
105 higher values both for the road-proximal side of the tree and for trees growing on the
106 uphill side of road lanes. These authors estimated the grain size of magnetic particles
107 from vehicle emissions to be of the order of 0.3 – 3 μm , a size of particular potential
108 hazard to health. Subsequent studies (e.g. Muxworthy et al., 2002; Moreno et al.,
109 2003; Hanesch et al., 2003; Gautam et al. 2005) have confirmed that, in the absence of
110 heavy industry, traffic pollution is the main source of magnetic particles on leaves.

111 Here, we report new data from the Norwich magnetic biomonitoring study,
112 with the aim of evaluating if magnetic biomonitoring can be used as a robust
113 surrogate for identifying the source and concentrations of toxic trace metals,
114 especially Pb.

115

116 2. Methods.

117 Over an 8-day, predominantly dry summer period, 100s of leaves were
118 sampled from the most abundant urban tree in Norwich, the birch (*Betula pendula*).
119 Following Matzka & Maher's original (1999) study, samples were taken from Grapes
120 Hill, a dual carriageway with a 12° gradient, part of the city's inner ring road.
121 Around 30,000 vehicles use this road each day (Norwich City Council, 1995). Birch
122 trees are planted in pairs along the central reservation area, providing uphill-adjacent
123 and downhill-adjacent trees. Each sample consisted of six leaves, sampled from the
124 outer canopy at a height of 1.5 m; the oldest leaves from the newest twig growth were
125 sampled, in order to ensure leaves of similar age and exposure time. In addition, leaf

126 samples were taken from one of the Grapes Hill birch trees at 30 cm intervals, from
127 the ground to a maximum height of 2.1 m. The surface area of the leaves was
128 calculated by digitizing their computer-scanned images. Leaves were then packed into
129 10 cc plastic sample holders for magnetic measurements, at the Centre for
130 Environmental Magnetism and Palaeomagnetism. Magnetic susceptibility was too
131 low to be measurable for any of the samples. All samples were magnetized (at room
132 temperature) with incremental, pulsed dc fields of 20, 50, 100 and 300 milliTesla
133 (mT) and 1 Tesla (T), using a Molspin Pulse Magnetiser. The resultant isothermal
134 (i.e. room temperature) magnetic remanences (IRMs) were measured using a
135 cryogenic magnetometer (CCL Ltd., with a noise level of 10^{-10} Am² – the weakest leaf
136 samples had remanences of the order of 10^{-8} Am²). A description of environmental
137 magnetic parameters and measuring techniques is given in e.g. Maher et al. (1999).
138 Selected samples were also subjected to af demagnetization; coercivity of magnetic
139 remanence was determined from the intersection of the IRM acquisition and
140 demagnetisation curves (higher values indicating magnetically harder behaviour, in
141 turn related to magnetic mineralogy and/or magnetic grain size).

142 A representative subset of samples was then selected for leaching and
143 elemental analysis. The leaves were leached in 25 ml 1 % HNO₃ and left in covered
144 bottles for 72 hours. Prior to use, all glass and plastic ware was washed with
145 detergent, soaked in 1 % HNO₃ for 24 hours and rinsed with high-purity ‘MilliQ’
146 water. The leaves were then recovered and their remanence at 1 T remeasured, in
147 order to identify the proportion of SIRM removed by the leaching procedure. Sample
148 leachates were filtered through 0.2 µm filters and then analysed by ICPOES (Thermo
149 Jarel Ash Polyscan 61E) for: Fe, Pb, Zn, Mn, Ba, Cd and Cr. (Elemental limits of
150 detection for this instrument are listed in Table 1). For each sample, the magnetic

151 remanences and elemental concentrations were normalized for leaf area, giving
152 magnetic moment (Am^2) per leaf area (m^2) – hence, in units of Amperes (A), and
153 elemental concentrations in units of $\mu\text{g}/\text{m}^2$. Further selected leaf samples were
154 vacuum-coated in gold and analysed using scanning electron microscopy (Hitachi
155 SEM S450) and energy-dispersive x ray analysis (EDXA). A small number of
156 samples was placed in plastic bottles with filtered ‘MilliQ’ water and treated
157 ultrasonically, to remove surface particulates. The suspensate was then sampled for
158 analysis using transmission electron microscopy (JEOL 100CX). Finally, air filter
159 samples were obtained from the background site (200 m^3 of air sampled) and the
160 closest possible site to the roadside (150 m^3 of air sampled, within 500 m of the
161 roadside), using a high-volume air sampler, and SIRM measurements made of the
162 filters.

163

164 3. Results.

165 Figure 1 shows the spatial variation in birch leaf magnetic values across the
166 urban-rural gradient, with very low SIRMs measured for leaves sampled from the
167 Norfolk coast and increasingly high values obtained for leaves with increasing
168 proximity to the roadside. For the leaves sampled over an 8-day summer period from
169 Grapes Hill, a major dual carriageway close to the Norwich city centre, the average,
170 leaf area-normalised (2-D) SIRM value (i.e. the remanence acquired at the maximum
171 applied dc field, 1 T) was $48.5 \cdot 10^{-6} \text{ A}$ (minimum = $27.5 \cdot 10^{-6} \text{ A}$, maximum = $96.1 \cdot 10^{-6}$
172 A). This compares with a background value (from trees sampled at a parkland site) of
173 $3.6 \cdot 10^{-6} \text{ A}$ (Table 1). Most of the leaf magnetic remanence was acquired at low
174 applied dc fields, indicating the presence of magnetically soft, magnetite-like (Fe_3O_4)
175 material. A small proportion of the remanence (< 5 % of the SIRM) was acquired at

176 fields beyond 300 mT, indicating the additional (and possibly volumetrically more
177 important) presence of magnetically 'hard' minerals, such as haematite ($\alpha\text{Fe}_2\text{O}_3$).
178 Coercivity values for the roadside leaves varied over a narrow range, from 42 – 46
179 mT, slightly higher than for the background samples, which displayed lower and
180 slightly more variable values, 35 – 42 mT. The magnetic data indicate that the
181 dominant size of the magnetic particles is between $\sim 1 - 0.1 \mu\text{m}$.

182 To examine the spatial variations in roadside SIRM and metal values, leaves
183 were collected from two birch trees within the central reservation, i.e. between the
184 uphill and downhill lanes of the Grapes Hill dual carriageway (fig. 2) following the
185 approach described by Matzka & Maher (1999). As reported previously by Matzka &
186 Maher (1999), SIRM values were again always highest for samples from both sides of
187 the uphill-adjacent tree, with slightly lower values for the road-proximal side of the
188 downhill-adjacent tree and lowest values for the distal side of the downhill-adjacent
189 tree (fig. 2b).

190 For the leaf leachates (Table 1), Zn and Fe were found to show the highest
191 roadside concentrations, with Mn, Ba and Pb at lower levels, and Cd and Cr below
192 their detection limits at all sampled sites. Background values for Fe and Pb were
193 minimal ($11 \mu\text{g}/\text{m}^2$ and below detection, respectively), in major contrast to the Grapes
194 Hill roadside sites, where Fe values averaged $427 \mu\text{g}/\text{m}^2$ (max. = $983 \mu\text{g}/\text{m}^2$), with an
195 average enhancement factor of x 39, and Pb values averaged $29 \mu\text{g}/\text{m}^2$ (max. = 81
196 $\mu\text{g}/\text{m}^2$, undetectable at background). Of the other analysed elements, Zn, Mn and Ba
197 all displayed significant concentrations even at the background sites ($\sim 119, 81$ and 54
198 $\mu\text{g}/\text{m}^2$, respectively). Their enhancement factors at the roadside were thus
199 correspondingly lower, at x 4, x 3 and x 1.5, respectively (Table 1). Demonstrating the
200 effectiveness of the analytical procedures, remagnetisation of a subset of leaf samples

201 after the leaching process showed that it had removed ~ 75 % of the original magnetic
202 remanence; the acid leach treatment (1 % HNO₃) is reported to remove up to 80 % of
203 total Pb, Zn and Cd (Little, 1973).

204 Thus, compared with the ‘background’, parkland site, the leaf SIRM, Pb and
205 Fe values show the greatest roadside enrichment. Lower roadside enrichment factors
206 are evident for Zn, Mn and Ba, reflecting their significant concentrations even at the
207 ‘background’ greenfield site. In terms of spatial variations across the Grapes Hill dual
208 carriageway, Fe and Pb concentrations display very similar patterns to the leaf SIRM
209 values, being highest at the uphill-proximal sample site (fig. 2c and d). Zn, Mn and
210 Ba values display greater spatial variation than Fe and Pb, with some maximal values
211 associated with the downhill-proximal samples. Leaf SIRM and metal values were
212 reduced (by between ~ 5 to 30 %) after a rainstorm event (the night of the second
213 sampling day), before subsequently increasing once more in the following dry
214 weather conditions. Table 2 shows the correlation coefficients (R² values) for the
215 measured leaf SIRM values and the elemental concentrations from the leaf leachates.
216 Very strong correlation is evident between the SIRM and concentrations of Fe (R² =
217 0.976, n = 40, p = < 0.05) and Pb (R² = 0.871). Significant albeit weaker correlation
218 (R² = 0.4 – 0.5) exists between the measured Zn, Mn and Ba concentrations. No
219 significant correlation exists between this group and the SIRM, Pb, Fe group.

220 Analysis of roadside leaves sampled at different heights showed that leaf
221 particulate Pb, Fe and SIRM concentrations reached peak values at ~ 0.3 m and 1.5 –
222 2 m above ground level (figure 3). In contrast, Zn, Ba and Mn displayed lowest
223 values at 0.3 m height, and steadily increased in concentration with height, indicating
224 (together with their higher background values) a more pervasive distribution of these
225 metals. The results were replicated over several days of sampling.

226 Scanning and transmission electron microscopy (STEM), and energy-
227 dispersive x ray analysis (EDXA), were applied to pollutant particles washed from the
228 sampled birch leaves from Grapes Hill. Two types of particle morphology were most
229 frequently observed: clusters of spheres (cooled droplets), ranging in size from ~ 20
230 μm to $< 0.5 \mu\text{m}$ (figure 5), and angular particles, between 1 and 10 μm in length.
231 Energy-dispersive x ray analysis of the spheres identified their major elements as Fe,
232 Si and Al, with varying concentrations of minor elements, including Mn, K, Ca and
233 Pb. Notably, Pb appeared to be associated only with the smallest spherules, $< \sim 1 \mu\text{m}$.
234 The angular particles were Fe-rich, some particles also containing S, Al, K and Ca.
235 Minor numbers of fine, irregular particles ($\sim 1 \mu\text{m}$ diameter) were also observed,
236 dominantly containing Ba, S and Mn. Finally, large conglomerates of particles (> 50
237 μm diameter) were also observed, dominantly consisting of Al, K, Ca and Si; such
238 particles are most likely of natural origin, probably soil-derived dust. Notably, few of
239 the analysed particles revealed the presence of zinc, even for leaf samples at sites
240 where the measured levels of Fe and Zn were comparable. Zinc oxide particles
241 derived from rubber dust have been shown to occur as ovoid particles of $< 0.5 \mu\text{m}$
242 (McCrone & Delly, 1973) - such particles would be resolvable under TEM. The
243 particles analysed here by STEM and EDXA were obtained by washing and ultrasonic
244 dispersion of the leaf surfaces; the absence of Zn-containing particles in these
245 suspensates but their presence in the acid leachates suggests significant incorporation
246 within the leaf cell structure by foliar penetration through the guard cells and cuticle
247 (Little, 1973).

248 Finally, in order to check how representative the tree leaves are as pollution
249 collectors, samples were also collected using a high volume air sampler, adjacent to a
250 roundabout at the top of the monitored dual carriageway and at the background site.

251 The sample nearest to the roadside gave rise to 3 x higher magnetic values per m³
252 sampled air than the background site, and its magnetic properties matched those of the
253 measured tree leaves.

254

255 4. Discussion

256 Roadside tree leaves in this UK city exhibit significant enhancement in their
257 values of SIRM, Fe and Pb, reflecting surface accumulation of particulate pollutants,
258 compared with leaves growing at a background, parkland site. In contrast, much more
259 limited roadside enhancement is shown by the metal group, Zn, Mn and Ba. At high
260 spatial resolution, maximal and strongly correlated Pb, Fe and SIRM values are
261 displayed by roadside tree leaves adjacent to uphill rather than downhill lanes. This
262 association between pollutant loading and road gradient indicates fuel combustion is
263 the major pollutant source; these patterns would not arise from resuspension of
264 roadside dust (Filippelli et al., 2005) or from tyre, brake or other vehicle wear. The
265 correlation between the SIRM values and leaf Pb concentrations is even stronger than
266 that observed between Pb and Fe. This suggests that Pb is strongly source-associated
267 with the magnetic Fe particulates, which arise from vehicle combustion/exhaust
268 processes, and less associated with more weakly magnetic phases either of natural
269 origin and/or from vehicle ablation or abrasion. The strong link between SIRM and
270 Pb could reflect coprecipitation of Pb during magnetite genesis (i.e. during
271 combustion) and/or subsequent adsorption of Pb on the surface of the combustion-
272 formed magnetic grains. Olson & Skogerboe (1975) previously reported that lead
273 emitted from vehicle exhausts occurs primarily in particulate form. This present-day
274 co-association of significant levels of automotive Pb and magnetic Fe emissions is
275 evident despite the introduction of unleaded petrol (in the UK, since 1986). Possible,

276 non-fuel, sources of Pb which could give rise to these ongoing, combustion-related
277 emissions include lead plating of fuel tanks, and lead in vulcanised fuel hoses, piston
278 coatings, valve seats and spark plugs. Pb is a significant neurotoxin, posing some
279 health risk at any level of exposure, particularly with regard to brain and kidney
280 damage, hearing impairment and cognitive development in children. Given the high
281 correlation coefficients between SIRM and Pb, SIRM values (measurements made
282 easily, rapidly and cheaply) appear valuable as a robust proxy predictor, and capable
283 of providing unprecedentedly high spatial resolution data, for this toxic pollutant.

284 Strong correlation also exists between SIRM and Fe content for the Grapes
285 Hill roadside sites, confirming the ferrimagnetic nature of much of the particulate Fe.
286 Based on the strong, direct linear relationship between SIRM and Fe concentration at
287 the roadside, when SIRM = 0, the Fe concentration = $52 \pm 40 \mu\text{g}/\text{m}^2$. For the
288 suburban ‘background’ site, the Fe concentration on sampled leaves was $11 \mu\text{g}/\text{m}^2$.
289 This suggests that much of the ‘non-magnetic’ Fe at the Grapes Hill sites is also
290 pollution-derived, from surface reception of non-magnetic iron compounds (e.g.
291 abraded rust particles). However, the ‘non-magnetic’ portion of the roadside Fe
292 content is only 11 % of the total.

293 Background levels of Zn, Mn and Ba are much higher than those for Fe and
294 Pb, resulting in enrichment ratios at the roadside of only 1.6 – 4 (compared with $\times 43$
295 and ∞ for Fe and Pb, respectively). The height distribution of the Zn, Mn and Ba
296 group, displaying increased elemental concentrations with height (up to the maximum
297 sampled height, 2.1 m), is again in contrast with the SIRM, Pb and Fe distributions,
298 which peak at ~ 0.3 m, with a subsidiary peak $\sim 1.5 - 2$ m height. These data suggest
299 that more pervasive, broader-scale atmospheric deposition processes are of
300 importance for ambient Zn, Mn and Ba levels. However, they do display some limited

301 degree of roadside enrichment and significant (albeit weaker) correlation between
302 them suggests some source association. The absence of correlation between the
303 SIRM, Fe and Pb data and the Zn, Mn, Ba group indicates different, non exhaust-
304 related sources for the latter at the Grapes Hill site. Across the dual carriageway, their
305 spatial variations are less systematic than those of Fe and Pb, but there is some
306 evidence of enhancement at the downhill-proximal sample site, suggesting braking
307 and tyre wear as significant sources. Huhn et al. (1995) have identified vehicle brake
308 and tyre wear as possible sources of Zn. Additionally, Ba is added to diesel fuel as a
309 smoke suppressant and Mn is used as an anti-knock agent (Huhn et al., 1995).

310 The peak SIRM, Pb and Fe values at ~ 0.3 m height are likely to reflect
311 exhaust-derived particulate emissions but it is possible that leaf drip from higher parts
312 of the canopy may make a contribution. Local weather conditions, rainsplash, and the
313 aerodynamic properties of the tree and its canopy, may also play a role in the height-
314 distribution of particulate deposition. As raindrops contain particles collected from
315 the atmosphere, they may contribute either to the accumulation of dust on leaf
316 surfaces or, by detaching previously collected particles, to its reduction. Here, rainfall
317 events led to reductions in the measured leaf SIRM and metal concentrations, whilst
318 dry conditions were associated with cumulative increases in leaf pollutant loadings.
319 This suggests that the main physical process responsible for particulate deposition is
320 impaction. Due to their inertia and/or density, particles cannot follow the air flow
321 around the leaves and consequently impact or sediment upon them (QUARG, 1996).
322 Deposited particles must also resist possible resuspension by turbulence; smaller
323 particles may penetrate more deeply into less exposed areas of the leaf surface
324 (Kinnersley et al., 1996).

325 For the metals analysed here, the highest roadside concentrations were found
326 for Fe (mean = 427 $\mu\text{g}/\text{m}^2$, max. = 742 $\mu\text{g}/\text{m}^2$) and Zn (mean = 468 $\mu\text{g}/\text{m}^2$, max. =
327 968 $\mu\text{g}/\text{m}^2$), both metal pollutants thought to be implicated in generating pulmonary
328 inflammation (e.g. Aust et al., 2002; Samet et al., 1998). Notably, even with Zn
329 loadings as high as here, the sampled leaves themselves showed no visible signs of
330 damage (a finding similar to that reported previously by Little, 1973).

331

332 We can use the strong, direct correlation between Pb and SIRM to estimate Pb
333 loadings per m^3 of air at this roadside. At the mean SIRM kerbside enhancement ratio
334 of 16 x background, roadside Pb levels equate to 13 ng/m^3 ; at the maximum SIRM
335 enhancement, the Pb concentration is 25 ng/m^3 . These estimated Pb concentrations
336 are comparable with levels recorded by the U.K.'s Air Quality Network for locations
337 including Manchester and Swansea. Critically, however, we show here that the
338 vehicle-derived Pb is associated with ultrafine ($< 1 \mu\text{m}$) magnetic particulates. Such
339 ultrafine grains, comprising very large particle numbers ($\sim 10^6 - 10^9 / \mu\text{g}$), pose
340 greatest health hazard. Their deposition in the lung may overwhelm the capacity of
341 macrophages to engulf and remove them, leading to prolonged tissue contact times
342 and resultant inflammation, whilst their high surface area also enhances their potential
343 for bioavailability (Donaldson, 2003). That roadside lead emissions are bioavailable is
344 indicated by reports of increased ^{210}Pb -supported ^{210}Po on the outer enamel of
345 permanent teeth in children living in proximity to ($< 10 \text{ km}$) and downwind from
346 major UK motorways (Henshaw et al., 1995; James et al., 2004). Further, interactions
347 between Fe-rich particles and epithelial tissues are suggested to generate free radicals,
348 leading to oxidative cell damage (Aust et al., 2002). Ultrafine particulates are likely
349 to pose a particular hazard to small children, doubly vulnerable because of

350 developmental health impacts and the measured peak in particulates at low heights, ~
351 0.3 m above ground (the secondary peak in Pb, Fe and SIRM values is close to head
352 height for most adults). Exposure may occur both at the roadside and/or within the
353 passenger cab of vehicles using the road.

354

355 Conclusions

- 356 • Urban roadside tree leaves exhibit significant enhancement in their
357 values of SIRM, Fe and Pb, reflecting surface accumulation of
358 particulate pollutants, compared with leaves growing at a background,
359 parkland site. Much more limited roadside enhancement is shown by
360 the metal group, Zn, Mn and Ba.

- 361
- 362 • Maximal (and strongly correlated) Pb, Fe and SIRM values are
363 displayed by roadside tree leaves adjacent to uphill rather than
364 downhill lanes. This association between pollutant loading and road
365 gradient indicates vehicle fuel combustion as the major source for
366 these pollutants, rather than resuspension of roadside dust or from tyre,
367 brake or other vehicle wear.

- 368
- 369 • The vehicle-derived Pb appears strongly associated with ultrafine (< 1
370 µm) magnetic particulates. Such ultrafine grains, contributing very
371 large particle numbers ($\sim 10^6 - 10^9 / \mu\text{g}$) and optimal bioavailability,
372 pose greatest hazard to human health.

373

- 374
- Ultrafine particulates pose a particular hazard to small children, doubly
375 vulnerable because of developmental health impacts and the
376 identification here of a peak in magnetic, Pb- and Fe-rich particulates
377 at child height (~ 0.3m above ground).
- 378
- Given the high correlation coefficients between Pb and leaf magnetic
379 values, easy, rapid and cheap magnetic measurements of roadside
380 leaves appear valuable as a robust proxy predictor of this toxic
381 pollutant, offering the possibility of greatly enhanced spatial resolution
382 of pollutant datasets, a prerequisite for detailed analysis of possible
383 pollution/health linkages (Schwarze et al., 2006).
- 384
- On an immediately practical level, this study suggests first, that
385
386 pedestrians can reduce their vehicle-derived pollution intake by
387 walking on the downhill side of the road, where possible with
388 intervening trees, and second, that the pollutant-filtering effects of
389 roadside trees would be significantly enhanced if tree-planting were
390 increased and lower-level leaf growth maintained, not removed.
- 391
- 392

393 References.

394 Abdul-Razzaq, W., Gautam, M., 2001. Discovery of magnetite in the exhausted
395 material from a diesel engine. *Applied Physics Letters* 78, 2018-2019.

396 Aust, A., Ball, J.C., Hu, A.A., Lighty, J.S., Smith, K.R., Straccia, A.M., Veranth,
397 J.M., Young, W.C., 2002. Particle characteristics responsible for effects on human
398 lung epithelial cells. Research Report 110, Health Effects Institute, Boston Ma.

399 Beeson, W.L., Abbey, D.E., Knutsen, S.F., 1998. Long term concentrations of
400 ambient air pollutants and incident lung cancer in Californian adults: results from the
401 AHSMOG study. *Environmental Health Perspectives* 106, 813-822.

402 Calderón-Garcidueñas, L., Reed, W., Maronpot RR, Henríquez-Roldán C, Delgado-
403 Chavez R, Calderón-Garcidueñas A, Dragustinovis, I., Franco-Lira, M., Aragón-
404 Flores, M., Solt, A.C., Altenburg, M., Torres-Jardón, R., Swenberg, J.A., 2004. Brain
405 inflammation and Alzheimer's-like pathology in individuals exposed to severe air
406 pollution. *Toxicology Pathology* 32(6), 650-8.

407 Colls, J. (2002). *Air pollution*. 2nd edition, Spon Press, London.

408 Donaldson, K., 2003. The biological effects of coarse and fine particulate matter.
409 *Occupational Environmental Medicine* 60, 313.

410 Filippelli, G.M., Laidlaw, M.A.S., Latimer, J.C. & Raftis, R., 2005. Urban lead
411 poisoning and medical geology: an unfinished story. *GSA Today* 15, 4-11.

412 Flanders, P.J., 1994. Collection, measurement, and analysis of airborne magnetic
413 particulates from pollution in the environment, *Journal Applied Physics* 75, 5931-
414 5936.

415 Gautam, P., Blaha, U. Appel, E., 2005. Magnetic susceptibility of dust-loaded leaves
416 as a proxy for traffic-related heavy metal pollution in Kathmandu city, Nepal.
417 *Atmospheric Environment* 39, 2201-2211.

418 Hanesch M, Scholger R, Rey D., 2003. Mapping dust distribution around an industrial
419 site by measuring magnetic parameters of tree leaves. *Atmospheric Environment* 37,
420 5125–5133.

421 Harrison, R.M., Jones, M., 1995. The chemical composition of airborne particles in
422 the UK atmosphere. *Science Total Environment* 168, 195-214.

423 Henshaw, D.L., Keitch, P.A. & James, P.R. 1995. Lead-210, polonium-210, and
424 vehicle exhaust pollution. *Lancet* 345, 324-325.

425 Huhn, G., Schulz, H., Staerk, H.J., Toelle, R. & Scheuermann, G., 1995. Evaluation of
426 regional heavy metal deposition by multivariate analysis of element contents in pine
427 tree barks. *Water, Air, Soil Pollution* 84, 367-383.

428 A. Hunt, J. Jones, F. Oldfield, 1984. Magnetic measurements and heavy metals in
429 atmospheric particulates of anthropogenic origin, *Science Total Environment* 33,
430 129-139.

431 James, P.R, Close J.J., Keitch, P.A., Allen, J.E., Fews, A.P., Henshaw D.L., 2004.
432 Aspects of the geographical variations of naturally occurring $^{210}\text{Pb}/^{210}\text{Po}$ in permanent
433 teeth of juveniles in the UK. *International Journal of Radiation Biology*, 80, 199-208.

434 Keyser, T. R., Natusch, D. F. S., Evans, C. A. Jr., Linton, R. W., 1978. Characterizing
435 the surfaces of environmental particles. *Environmental Science Technology* 12(7),
436 768 - 773

437 Kinnersley, R.P., Shaw, G., Bell, J.N.B, Minski, M.J., Goddard, A.J.H., 1996. Loss of
438 particulate contaminants from plant canopies under wet and dry conditions.
439 *Environmental Pollution* 91, 227–235.

440 Koller, K., Brown, T., Spurgeon, A., Levy, L., 2004. Recent developments in low-
441 level lead exposure and intellectual impairment in children. *Environment Health*
442 *Perspectives* 112, 987-994.

443 Knox, E.G., 2006. Roads, railways and childhood cancers. *Journal Epidemiology and*

444 Community Health 60, 136-141.

445 Knutsen, S., Shavlik, D., Chen, L.H., Beeson, W.L., Ghamsary, M., Petersen, F.,
446 2004. The association between ambient particulate air pollution levels and risk of
447 cardiopulmonary and all-cause mortality during 22 years follow-up of a non-smoking
448 cohort. Results from the AHSMOG study. *Epidemiology*, 15 S45-S45.

449 Lanphear B.P., Dietrich K., Auinger, P., Cox, C., 2000. Deficits in cognitive and
450 academic skills associated with lead exposure occur at blood lead concentrations
451 lower than 5 microg/dL. *Public Health Report* 115, 530-531.

452 Little, P., 1973. A study of heavy metal contamination of leaf surfaces. *Environmental*
453 *Pollution* 5, 159-172.

454 Maher, B.A., Thompson, R. & Hounslow, M.W. (1999) Introduction to Quaternary
455 Climates, Environments and Magnetism. In Maher, B.A. & Thompson, R. (eds.),
456 Quaternary Climates, Environments and Magnetism, Cambridge University Press, 1-48.

457 Maricq, M., 1999. Examination of the size-resolved and transient nature of motor
458 vehicle particle emissions. *Environmental Science Technology* 33, 1618-1626.

459 Mathee, A., Schirnding, Y.E.R., Levin, J., Ismail, A., Huntley, R., Cantrell, A.A.,
460 2002. A survey of blood lead levels among young Johannesburg school children.
461 *Environmental Research* 90, 181-184.

462 Matzka, J., Maher, B.A., 1999. Magnetic biomonitoring of roadside tree leaves:
463 identification of spatial and temporal variations in vehicle-derived particulates.
464 *Atmospheric Environment* 33, 4565-4569.

465 McCrone, W.C., Delly, J.G., 1973. The particle atlas: volume 2, the light microscopy
466 atlas. Ann Arbor, Michigan USA.

467 Moreno, E., L. Sagnotti, J.D. Dinares-Turell, A. Winkler & A. Cascella, 2004.
468 *Atmospheric Environment* 37, 2967-77.

469 Morris W A. Morris, J. K. Versteeg, D. W. Bryant, A. E. Legzdins, B. E. McCarry &
470 C. H. Marvin, 1995. Preliminary comparison between mutagenicity and magnetic
471 susceptibility of respirable airborne particulates, *Atmospheric Environment* 29, 3441-
472 3450.

473 Muxworthy, A.R., Schmidbauer, E. & Petersen, N., 2002. Magnetic properties and
474 Mossbauer spectra of urban atmospheric particulate matter: a case study from
475 Munich, Germany. *Geophysical Journal International* 150, 558-570.

476 Needleman, H.L., Landrigan P., 2004. What level of lead in blood is toxic for a child?
477 (Letter) *American Journal Public Health* 94, 8.

478 Olson, K.W. & Skogerboe, R.K., 1975. Identification of soil lead compounds from
479 automotive sources. *Environmental Science Technology* 9, 227-230.

480 Petrovsky, E, Ellwood, B.B., 1999. Magnetic monitoring of pollution of air, land and
481 waters. In: Maher, B.A., Thompson, R. (Eds.), *Quaternary Climates , Environments*
482 *and Magnetism*, Cambridge University Press, Cambridge, pp. 279-322.

483 Pope, C.A. III, Thun, M.J., Namboodiri, M., Dockery, D.W., Evans, J.S., Speizer,
484 F.E., Heath, C.W., 1995. Particulate air pollution as a predictor of mortality in a
485 prospective study of U.S. adults. *American Journal Respiratory Critical Care*
486 *Medicine* 151,669-674.

487 Pope, C.A. III, Burnett, R.T.; Thun, M.J., Calle, E.E., Krewski, D., Kazuhiko I.,
488 Thurston, G.D., 2002. Lung Cancer, Cardiopulmonary Mortality, and Long-term
489 Exposure to Fine Particulate Air Pollution. *Journal American Medical Association*
490 287,1132-1141.

491 Quality of Urban Air Review Group, 1996. *Airborne Particle Matter in the United*
492 *Kingdom, QUARG 3rd report*, UK.

493 Rabito, F.A., Shorter, C., White, L.E., 2004. Lead levels among children who live in

494 public housing. *Epidemiology* 216, 263-268.

495 Rudell, B., Blomberg, A., Helleday, R., Ledin, M.C., Lundback, B., Stjernberg, N.,
496 Horstedt, P. & Sandstrom, T., 1999. Bronchoalveolar inflammation after exposure to
497 diesel exhaust: comparison between unfiltered and particle trap filtered exhaust.
498 *Occupational Environment Medicine* 56, 527-534.

499 Samet, JM, Graves, LM, Quay, J, Dailey, LA, Devlin, RB, Ghio, AJ, Weidong Wu,
500 Bromberg, PA and Reed, W., 1998. Activation of MAP kinases in human bronchial
501 epithelial cells exposed to metals. *American Journal Physiology Lung Cell Molecular*
502 *Physiology*, 275, 551-558.

503 Schadlich, G., Weissflog, L. & Schuurmann, G., 1995. Magnetic susceptibility in
504 conifer needles as indicator of fly ash deposition. *Fres. Enviro. Bull.* 4, 7-12.

505 Schwartz, J., 1996. Air pollution and hospital admissions for respiratory disease.
506 *Epidemiology* 7, 20-28.

507 Schwarze, P.E.; Øvrevik, J.; Låg, M.; Refsnes, M.; Nafstad, P.; Hetland,
508 R.B.; Dybing, E., 2006. Particulate matter properties and health effects: consistency of
509 epidemiological and toxicological studies. *Human and experimental toxicology*,
510 25, 559-579.

511 Seaton, A., MacNee, W., Donaldson, K., 1995. Particulate air pollution and acute
512 health effects. *Lancet* 345, 176-8.

513 Wang, Y.F., Huang, K.L, Li, C.T., Mi, H.H., Luo, J.H & Tsai, P.J., 2003. Emissions
514 of fuel metals content from a diesel vehicle engine. *Atmospheric Environment* 37,
515 4637-4643.

516 Young, T.M., Heerman, D.A., Sirin, G. & Ashbaugh, L.L., 2002. Resuspension of soil
517 as a source of airborne lead near industrial facilities and highways. *Environmental*
518 *Science Technology* 36, 2484-2490.

519 Figure captions.

520 Figure 1 Variation with location of 2-D magnetic remanence values (SIRMs),
521 measured on sampled birch leaves, from Weybourne on the Norfolk coast to the
522 central reservation of Grapes Hill, a major city centre dual carriageway.

523 Figure 2 Pb, Fe and 2-D SIRM values for tree leaves sampled across the central
524 reservation of the uphill and downhill lanes of a major dual carriageway (Grapes Hill)
525 in Norwich, U.K., a) sample locations, b) Pb concentrations, c) Fe concentrations, d)
526 2-D SIRM. Leaves were sampled over a predominantly dry summer period; heavy
527 rain fell overnight on days 3/4.

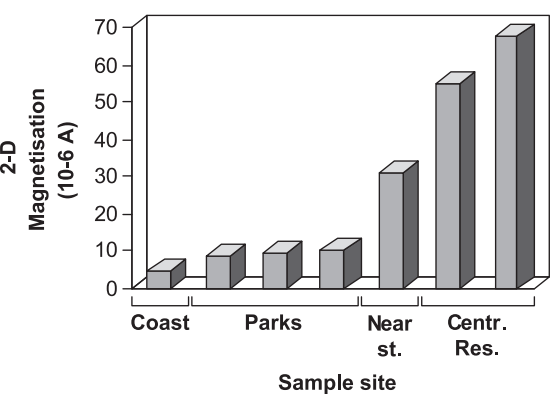
528 Figure 3 Correlations between leaf particulate metal concentrations and SIRM (n =
529 40, $p = < 0.05$), Grapes Hill, Norwich: a) all analysed metals and b) Pb concentration
530 and SIRM.

531 Figure 4 Variation with height of leaf particulate metal concentrations and SIRM.

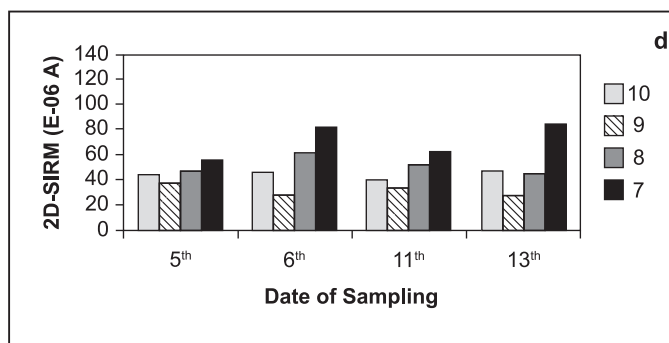
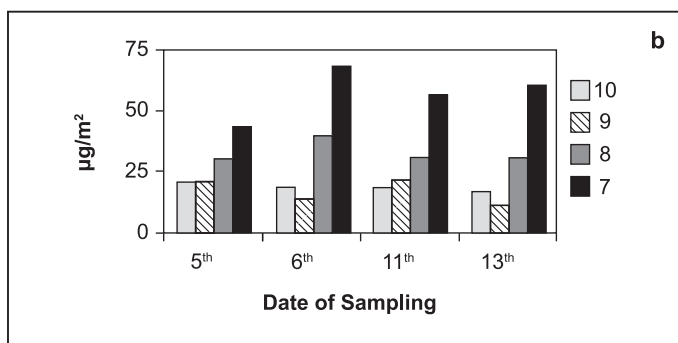
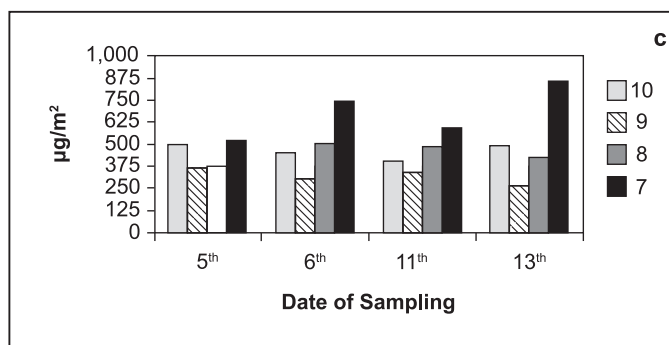
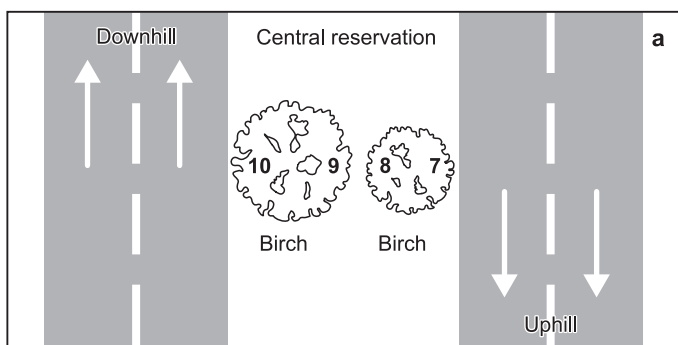
532 Figure 5 Scanning electron micrograph of clustered, spherical leaf particulates,
533 Grapes Hill, Norwich. From elemental analysis, Pb occurs as a minor element only
534 within the spherules $< 1 \mu\text{m}$ diameter.

535 Table caption
536 Table 1 Averaged elemental concentrations ($\mu\text{g}/\text{m}^2$) of leaf leachates and SIRM
537 (measured in applied dc field of 1 T and normalized for leaf surface area) for sampled
538 birch leaves from Grapes Hill and ‘background’ values from the campus of the
539 University of East Anglia. Samples were taken from 40 trees over a 5-day summer
540 period, with wind directions varying mainly within the range 210 – 240 °;
541 thunderstorms occurred overnight on sample days 2/3. Each data point represents a
542 measurement integrating over 6 leaves from each tree.

Figure



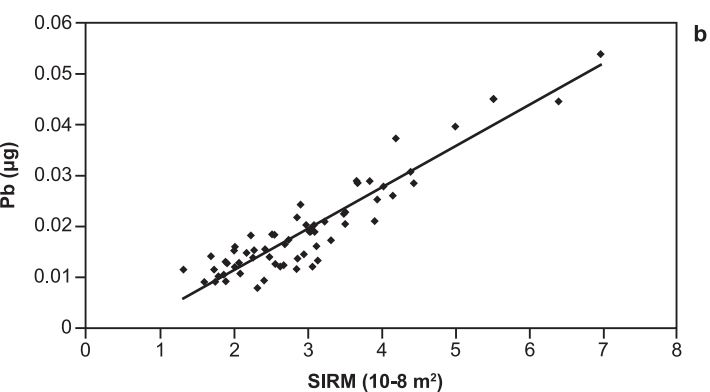
Figure



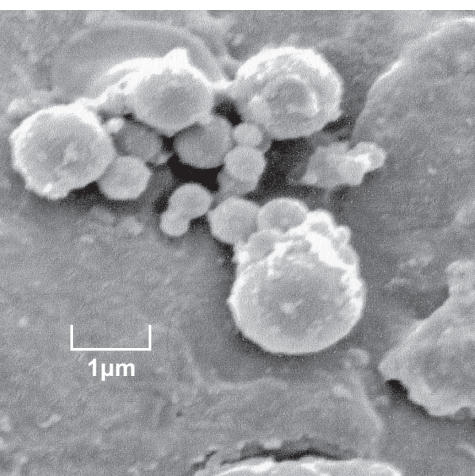
Figure

	SIRM	Fe	Pb	Zn	Mn	Ba
SIRM	1					
Fe	0.976	1				
Pb	0.871	0.849	1			
Zn	0.035	0.028	0.101	1		
Mn	0.009	0.014	0.014	0.444	1	
Ba	0.001	0.006	0.003	0.414	0.500	1

a



b



Figure

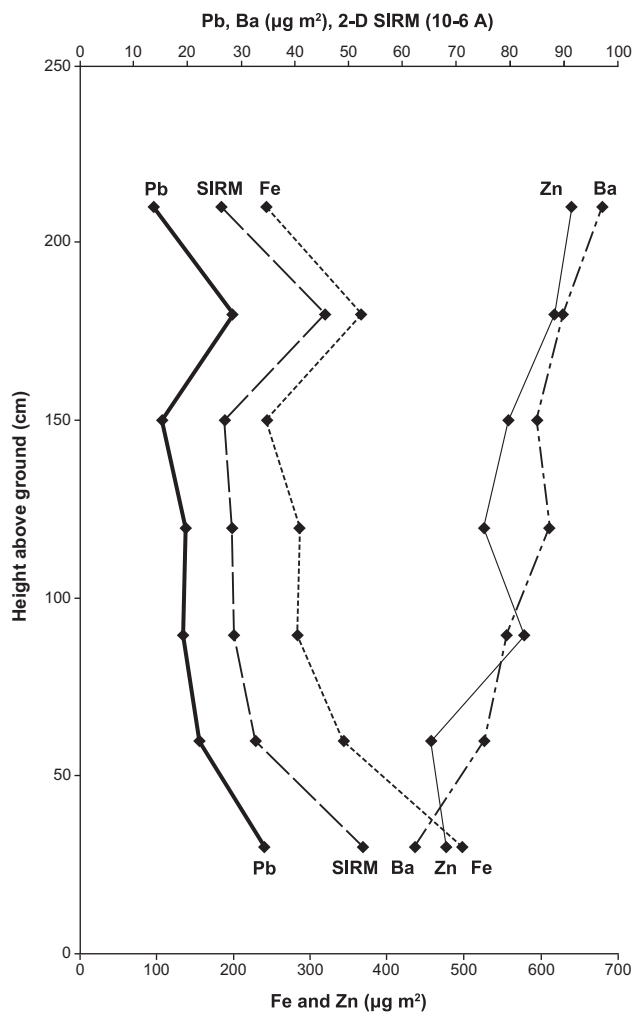


Table
[Click here to download Table: Maher et al Atmos Env Table 1.doc](#)

Element / SIRM	Roadside ($\mu\text{g}/\text{m}^2$)	Background ($\mu\text{g}/\text{m}^2$)	Mean enrichment ratio roadside: background	Detection limit ($\mu\text{g}/\text{m}^2$)
Pb	29	below limit		2.5
Fe	427	11	39	0.2
Zn	468	119	4	0.2
Mn	222	81	3	0.05
Ba	82	54	1.5	0.02
2-D SIRM (10^{-6} A)	48	3	16	10^{-10} A