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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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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 ☐ 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 under-estimate 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.

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

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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 (< 1μm) 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 under-estimate 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.

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

1. Introduction.

Particulate air pollutants have been found to be strongly associated with adverse effects on respiratory health (e.g. Knox, 2006; Knutsen et al. 2004, Schwartz, 1996; Pope et al., 2002). The degree of hazard depends principally on the site of particulate deposition within the lungs, in turn reflecting the size, shape and density of the particulates, and their effects on biological tissue, determined by the composition of the particles. Ultrafine particles (< 2.5 μm, $PM_{2.5}$) can be deposited deep within the pulmonary region of the human respiratory tract when inhaled, with potential bioavailability maximised by the large number and surface area of such particles. If these particulates reach the alveoli, inflammation and diminished pulmonary function can be incurred (e.g. Knutsen et al., 2004; Seaton et al., 1995). Links with lung cancer (Pope et al., 2002; Beeson et al., 1998) and increased cardiovascular mortality rates (Pope et al., 1995; Schwartz et al., 1996) have also been established. Large proportions of such ultrafine particles are known to be emitted by vehicles (e.g. Maricq, 1999), with diesel-powered vehicles producing several orders of magnitude more $PM_{2.5}$ particles than petrol-driven ones (Rudell et al., 1999; Maricq, 1999; Wang et al., 2003). In terms of composition, analysis of urban anthropogenic particulates has shown them to be enriched in a range of potentially toxic trace metals, including Fe, Pb, Zn, Ba, Mn, Cd and Cr (Huhn et al., 1995; Harrison & Jones, 1995). Keyser et al. (1978) reported that Pb and Cr from vehicle exhausts are preferentially associated with particle surfaces, possibly as a result of condensation from the vapour phase or adsorption from solution. Urban anthropogenic particulates also contain, almost invariably, magnetic particles (e.g. Hunt et al., 1984; Flanders, 1994; Morris et al., 1995; Matzka & Maher, 1999; Petrovsky & Ellwood, 1999). These derive from the presence of iron impurities in fuels, which form upon combustion a non-volatile residue, often a mix of strongly magnetic (magnetite-like) and weakly magnetic (haematite-like) iron oxides. Magnetite has been identified specifically as a combustion-derived component of vehicle exhaust materials (Abdul-Razzaq & Gautam, 2001).

Quantitatively, the health risks of urban metal particulates are poorly understood, due to a combination of confounding factors and the relatively low spatial resolution of the data available for pollutant exposure. However, Pb is a significant neurotoxin, posing some health risk even at levels previously considered safe, particularly with regard to brain and kidney damage, hearing impairment and diminished cognitive development in children (Koller et al., 2004; Lanphear et al., 2000; Needleman & Landrigan, 2004). High levels of many other trace metals are implicated in lung disease and central nervous system disorders (e.g. Colls, 2002), ranging from learning disorders to dementia and possibly even Alzheimers's disease (Calderón-Garcidueñas et al., 2004). Aggressive removal of lead from environmental sources, especially petrol and paints, has resulted in major reductions in lead poisoning of children. However, many urban areas still exhibit damagingly high blood lead levels (i.e. > 5µg/dl) in children (e.g. Koller et al., 2004; Lanphear et al., 2000; Mathee et al. 2002). In a study in the Indianapolis area, resuspended soil dust, enriched with lead from previous decades of leaded fuel usage, was the suspected major source, in light of higher blood lead levels at the urban roadside and seasonal peaks (summer and winter) in blood lead (Filippelli et al., 2005).

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

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

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

2. Methods.

Over an 8-day, predominantly dry summer period, 100s of leaves were sampled from the most abundant urban tree in Norwich, the birch (*Betula pendula*). Following Matzka & Maher's original (1999) study, samples were taken from Grapes Hill, a dual carriageway with a 12 ^{o} gradient, part of the city's inner ring road. Around 30,000 vehicles use this road each day (Norwich City Council, 1995). Birch trees are planted in pairs along the central reservation area, providing uphill-adjacent and downhill-adjacent trees. Each sample consisted of six leaves, sampled from the outer canopy at a height of 1.5 m; the oldest leaves from the newest twig growth were sampled, in order to ensure leaves of similar age and exposure time. In addition, leaf samples were taken from one of the Grapes Hill birch trees at 30 cm intervals, from the ground to a maximum height of 2.1 m. The surface area of the leaves was calculated by digitizing their computer-scanned images. Leaves were then packed into 10 cc plastic sample holders for magnetic measurements, at the Centre for Environmental Magnetism and Palaeomagnetism. Magnetic susceptibility was too low to be measurable for any of the samples. All samples were magnetized (at room temperature) with incremental, pulsed dc fields of 20, 50, 100 and 300 milliTesla (mT) and 1 Tesla (T), using a Molspin Pulse Magnetiser. The resultant isothermal (i.e. room temperature) magnetic remanences (IRMs) were measured using a cryogenic magnetometer (CCL Ltd., with a noise level of 10^{-10} Am^2 – the weakest leaf samples had remanences of the order of 10^{-8} Am^2). A description of environmental magnetic parameters and measuring techniques is given in e.g. Maher et al. (1999). Selected samples were also subjected to af demagnetization; coercivity of magnetic remanence was determined from the intersection of the IRM acquisition and demagnetisation curves (higher values indicating magnetically harder behaviour, in turn related to magnetic mineralogy and/or magnetic grain size).

A representative subset of samples was then selected for leaching and elemental analysis. The leaves were leached in 25 ml 1 % HNO_3 and left in covered bottles for 72 hours. Prior to use, all glass and plastic ware was washed with detergent, soaked in 1 % HNO_3 for 24 hours and rinsed with high-purity 'MilliQ' water. The leaves were then recovered and their remanence at 1 T remeasured, in order to identify the proportion of SIRM removed by the leaching procedure. Sample leachates were filtered through 0.2 μm filters and then analysed by ICPOES (Thermo Jarel Ash Polyscan 61E) for: Fe, Pb, Zn, Mn, Ba, Cd and Cr. (Elemental limits of detection for this instrument are listed in Table 1). For each sample, the magnetic remanences and elemental concentrations were normalized for leaf area, giving magnetic moment (Am^2) per leaf area (m^2) – hence, in units of Amperes (A), and elemental concentrations in units of $\mu g/m^2$. Further selected leaf samples were vacuum-coated in gold and analysed using scanning electron microscopy (Hitachi SEM S450) and energy-dispersive x ray analysis (EDXA). A small number of samples was placed in plastic bottles with filtered 'MilliQ' water and treated ultrasonically, to remove surface particulates. The suspensate was then sampled for analysis using transmission electron microscopy (JEOL 100CX). Finally, air filter samples were obtained from the background site (200 m^3 of air sampled) and the closest possible site to the roadside (150 m^3 of air sampled, within 500 m of the roadside), using a high-volume air sampler, and SIRM measurements made of the filters.

3. Results.

Figure 1 shows the spatial variation in birch leaf magnetic values across the urban-rural gradient, with very low SIRMs measured for leaves sampled from the Norfolk coast and increasingly high values obtained for leaves with increasing proximity to the roadside. For the leaves sampled over an 8-day summer period from Grapes Hill, a major dual carriageway close to the Norwich city centre, the average, leaf area-normalised (2-D) SIRM value (i.e. the remanence acquired at the maximum applied dc field, 1 T) was 48.5 10^{-6} A (minimum = 27.5 10^{-6} A, maximum = 96.1 10^{-6} A). This compares with a background value (from trees sampled at a parkland site) of 3.6 10^{-6} A (Table 1). Most of the leaf magnetic remanence was acquired at low applied dc fields, indicating the presence of magnetically soft, magnetite-like (Fe_3O_4) material. A small proportion of the remanence (< 5 % of the SIRM) was acquired at fields beyond 300 mT, indicating the additional (and possibly volumetrically more important) presence of magnetically 'hard' minerals, such as haematite (αFe_2O_3). Coercivity values for the roadside leaves varied over a narrow range, from 42 – 46 mT, slightly higher than for the background samples, which displayed lower and slightly more variable values, 35 – 42 mT. The magnetic data indicate that the dominant size of the magnetic particles is between ~1 – 0.1 μm.

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

For the leaf leachates (Table 1), Zn and Fe were found to show the highest roadside concentrations, with Mn, Ba and Pb at lower levels, and Cd and Cr below their detection limits at all sampled sites. Background values for Fe and Pb were minimal (11 $\mu g/m^2$ and below detection, respectively), in major contrast to the Grapes Hill roadside sites, where Fe values averaged 427 $\mu g/m^2$ (max. = 983 $\mu g/m^2$), with an average enhancement factor of x 39, and Pb values averaged 29 $\mu g/m^2$ (max. = 81 $\mu g/m^2$, indetectable at background). Of the other analysed elements, Zn, Mn and Ba all displayed significant concentrations even at the background sites (~ 119, 81 and 54 $\mu g/m^2$, respectively). Their enhancement factors at the roadside were thus correspondingly lower, at x 4, x 3 and x 1.5, respectively (Table 1). Demonstrating the effectiveness of the analytical procedures, remagnetisation of a subset of leaf samples after the leaching process showed that it had removed ~ 75 % of the original magnetic remanence; the acid leach treatment (1 % HNO_3) is reported to remove up to 80 % of total Pb, Zn and Cd (Little, 1973).

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

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

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

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

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

4. Discussion

Roadside tree leaves in this UK city exhibit significant enhancement in their values of SIRM, Fe and Pb, reflecting surface accumulation of particulate pollutants, compared with leaves growing at a background, parkland site. In contrast, much more limited roadside enhancement is shown by the metal group, Zn, Mn and Ba. At high spatial resolution, maximal and strongly correlated Pb, Fe and SIRM values are displayed by roadside tree leaves adjacent to uphill rather than downhill lanes. This association between pollutant loading and road gradient indicates fuel combustion is the major pollutant source; these patterns would not arise from resuspension of roadside dust (Filippelli et al., 2005) or from tyre, brake or other vehicle wear. The correlation between the SIRM values and leaf Pb concentrations is even stronger than that observed between Pb and Fe. This suggests that Pb is strongly source-associated with the magnetic Fe particulates, which arise from vehicle combustion/exhaust processes, and less associated with more weakly magnetic phases either of natural origin and/or from vehicle ablation or abrasion. The strong link between SIRM and Pb could reflect coprecipitation of Pb during magnetite genesis (i.e. during combustion) and/or subsequent adsorption of Pb on the surface of the combustion-formed magnetic grains. Olson & Skogerboe (1975) previously reported that lead emitted from vehicle exhausts occurs primarily in particulate form. This present-day co-association of significant levels of automotive Pb and magnetic Fe emissions is evident despite the introduction of unleaded petrol (in the UK, since 1986). Possible, non-fuel, sources of Pb which could give rise to these ongoing, combustion-related emissions include lead plating of fuel tanks, and lead in vulcanised fuel hoses, piston coatings, valve seats and spark plugs. Pb is a significant neurotoxin, posing some health risk at any level of exposure, particularly with regard to brain and kidney damage, hearing impairment and cognitive development in children. Given the high correlation coefficients between SIRM and Pb, SIRM values (measurements made easily, rapidly and cheaply) appear valuable as a robust proxy predictor, and capable of providing unprecedentedly high spatial resolution data, for this toxic pollutant.

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

Background levels of Zn, Mn and Ba are much higher than those for Fe and Pb, resulting in enrichment ratios at the roadside of only 1.6 – 4 (compared with x 43 and ∞ for Fe and Pb, respectively). The height distribution of the Zn, Mn and Ba group, displaying increased elemental concentrations with height (up to the maximum sampled height, 2.1 m), is again in contrast with the SIRM, Pb and Fe distributions, which peak at ~ 0.3 m, with a subsidiary peak ~ 1.5 – 2 m height. These data suggest that more pervasive, broader-scale atmospheric deposition processes are of importance for ambient Zn, Mn and Ba levels. However, they do display some limited degree of roadside enrichment and significant (albeit weaker) correlation between them suggests some source association. The absence of correlation between the SIRM, Fe and Pb data and the Zn, Mn, Ba group indicates different, non exhaust-related sources for the latter at the Grapes Hill site. Across the dual carriageway, their spatial variations are less systematic than those of Fe and Pb, but there is some evidence of enhancement at the downhill-proximal sample site, suggesting braking and tyre wear as significant sources. Huhn et al. (1995) have identified vehicle brake and tyre wear as possible sources of Zn. Additionally, Ba is added to diesel fuel as a smoke suppressant and Mn is used as an anti-knock agent (Huhn et al., 1995).

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

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

We can use the strong, direct correlation between Pb and SIRM to estimate Pb loadings per m^3 of air at this roadside. At the mean SIRM kerbside enhancement ratio of 16 x background, roadside Pb levels equate to 13 ng/m^3; at the maximum SIRM enhancement, the Pb concentration is 25 ng/m^3. These estimated Pb concentrations are comparable with levels recorded by the U.K.'s Air Quality Network for locations including Manchester and Swansea. Critically, however, we show here that the vehicle-derived Pb is associated with ultrafine (< 1 μm) magnetic particulates. Such ultrafine grains, comprising very large particle numbers (~ 10^6 –10^9 / μg), pose greatest health hazard. Their deposition in the lung may overwhelm the capacity of macrophages to engulf and remove them, leading to prolonged tissue contact times and resultant inflammation, whilst their high surface area also enhances their potential for bioavailability (Donaldson, 2003). That roadside lead emissions are bioavailable is indicated by reports of increased ^{210}Pb-supported ^{210}Po on the outer enamel of permanent teeth in children living in proximity to (< 10 km) and downwind from major UK motorways (Henshaw et al., 1995; James et al., 2004). Further, interactions between Fe-rich particles and epithelial tissues are suggested to generate free radicals, leading to oxidative cell damage (Aust et al., 2002). Ultrafine particulates are likely to pose a particular hazard to small children, doubly vulnerable because of developmental health impacts and the measured peak in particulates at low heights, ~ 0.3 m above ground (the secondary peak in Pb, Fe and SIRM values is close to head height for most adults). Exposure may occur both at the roadside and/or within the passenger cab of vehicles using the road.

Conclusions

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

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

- The vehicle-derived Pb appears strongly associated with ultrafine (< 1 μm) magnetic particulates. Such ultrafine grains, contributing very large particle numbers (~ 10^6 –10^9 /μg) and optimal bioavailability, pose greatest hazard to human health.

- Ultrafine particulates pose a particular hazard to small children, doubly vulnerable because of developmental health impacts and the identification here of a peak in magnetic, Pb- and Fe-rich particulates at child height (~ 0.3m above ground).

- Given the high correlation coefficients between Pb and leaf magnetic values, easy, rapid and cheap magnetic measurements of roadside leaves appear valuable as a robust proxy predictor of this toxic pollutant, offering the possibility of greatly enhanced spatial resolution of pollutant datasets, a prerequisite for detailed analysis of possible pollution/health linkages (Schwarze et al., 2006).

- On an immediately practical level, this study suggests first, that pedestrians can reduce their vehicle-derived pollution intake by walking on the downhill side of the road, where possible with intervening trees, and second, that the pollutant-filtering effects of roadside trees would be significantly enhanced if tree-planting were increased and lower-level leaf growth maintained, not removed.

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Figure captions.

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

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

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

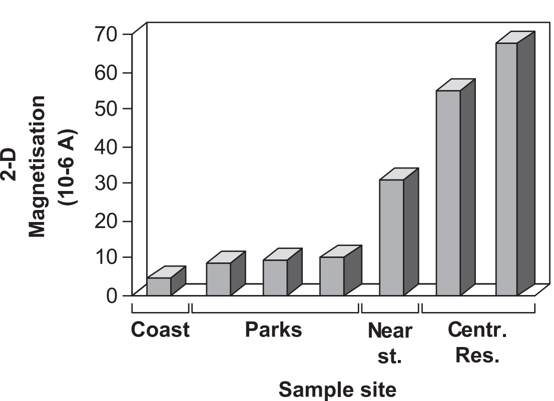
Figure 4 Variation with height of leaf particulate metal concentrations and SIRM.

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

Table caption

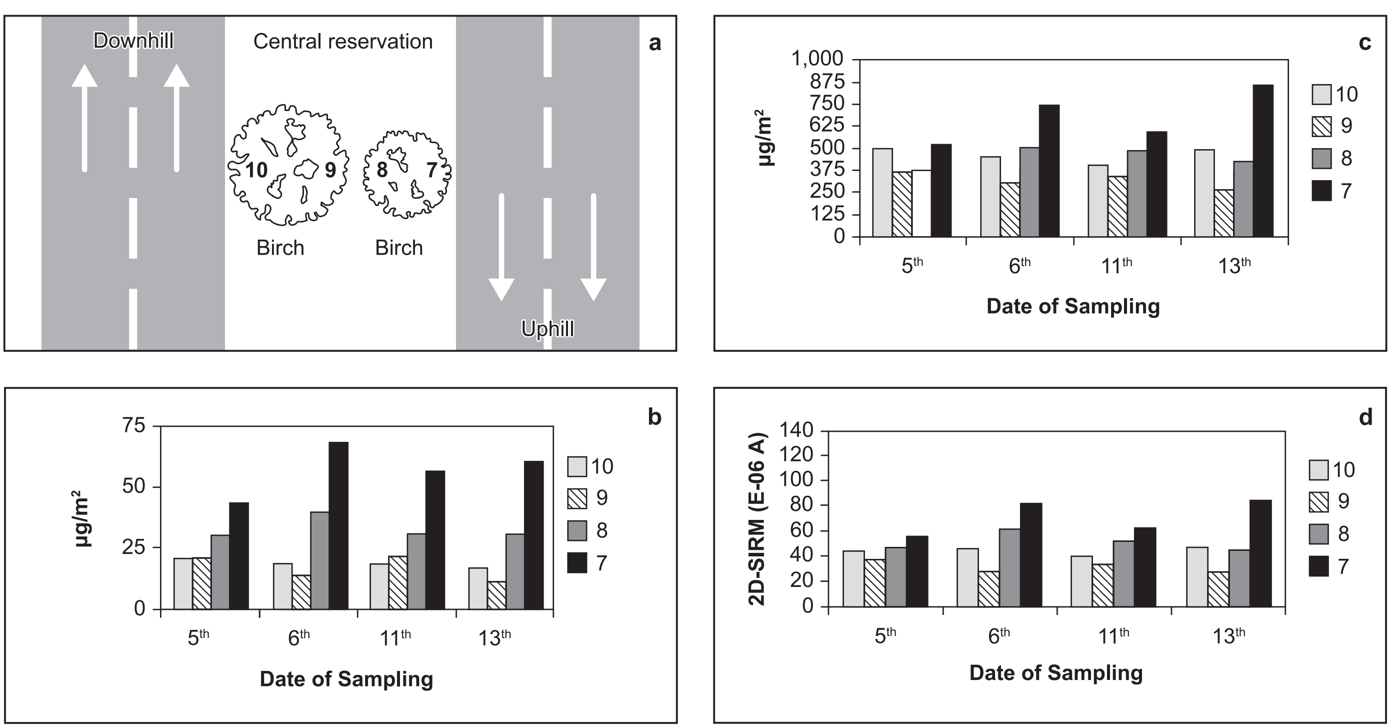
Table 1 Averaged elemental concentrations (μg/m^2) of leaf leachates and SIRM (measured in applied dc field of 1 T and normalized for leaf surface area) for sampled birch leaves from Grapes Hill and 'background' values from the campus of the University of East Anglia. Samples were taken from 40 trees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

Figure



2-D
Magnetisation
(10-6 A)
70
60
50
40
30
20
10
0
Coast
Parks
Near
st.
Centr.
Res.
Sample site

Figure

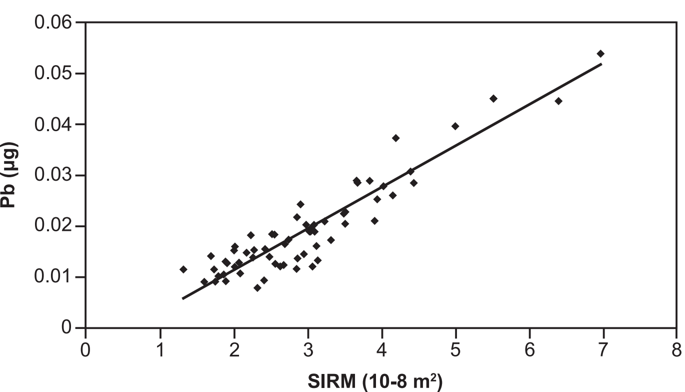


Downhill
Central reservation
a
10
9
8
7
Birch
Birch
Uphill
c
1,000
875
750
625
500
375
250
125
0
μg/m²
10
9
8
7
5th
6th
11th
13th
Date of Sampling
b
75
50
25
0
μg/m²
10
9
8
7
5th
6th
11th
13th
Date of Sampling
d
140
120
100
80
60
40
20
0
2D-SIRM (E-06 A)
10
9
8
7
5th
6th
11th
13th
Date of Sampling

Figure

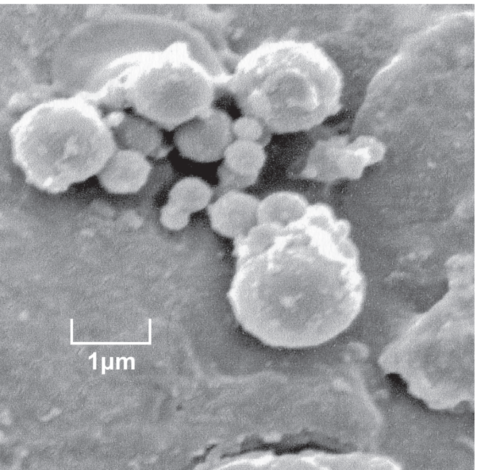
	SIRM	Fe	Pb	Zn	Mn	Ba
SIRM	1					
Fe	0.976	1				
Pb	0.871	0.849	1			
Zn	0.035	0.028	0.101	1		
Mn	0.009	0.014	0.014	0.444	1	
Ba	0.001	0.006	0.003	0.414	0.500	1

a

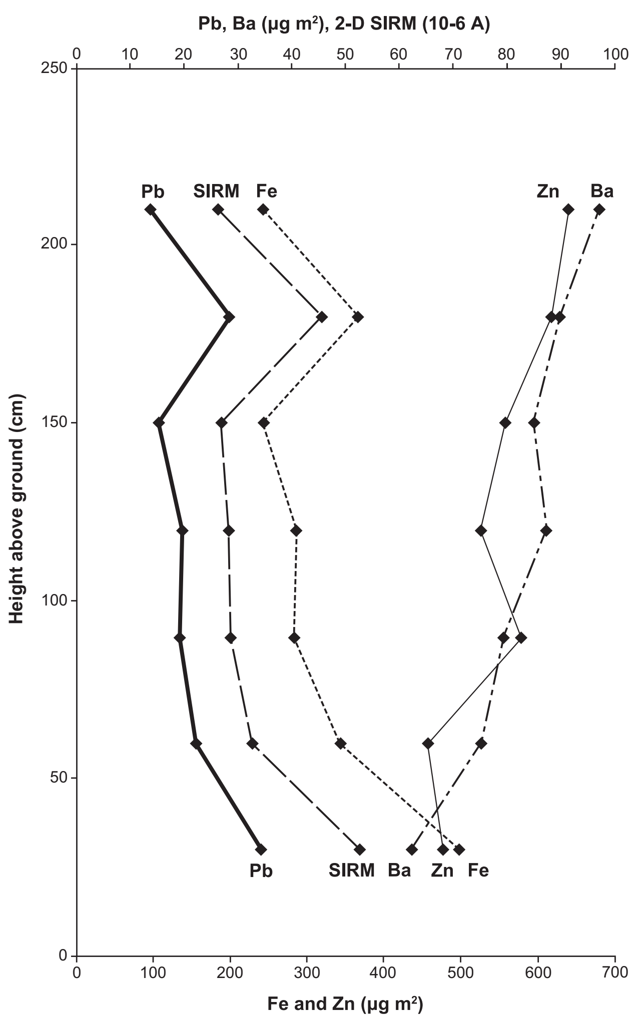


b

Figure



Figure


Pb, Ba (µg m²), 2-D SIRM (10-6 A)
0
10
20
30
40
50
60
70
80
90
100
250
200
150
100
50
0
Height above ground (cm)
Pb
SIRM
Fe
Zn
Ba
Pb
SIRM
Ba
Zn
Fe
0
100
200
300
400
500
600
700
Fe and Zn (µg m²)

Table

Element / SIRM	Roadside ($\mu g/m^2$)	Background ($\mu g/m^2$)	Mean enrichment ratio roadside: background	Detection limit (μg/m2)
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