

1 **Deposition and solubility of airborne metals to four plant species grown**
2 **at varying distances from two heavily trafficked roads in London**

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12

13 **Abstract**

14 In urban areas, a highly variable mixture of pollutants is deposited as particulate
15 matter. The concentration and bioavailability of individual pollutants within particles need to
16 be characterised to ascertain the risks to ecological receptors. This study, carried out at two
17 urban parks, measured the deposition and water-solubility of metals to four species common
18 to UK urban areas. Foliar Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations were elevated in at
19 least one species compared with those from a rural control site. Concentrations were,
20 however, only affected by distance to road in nettle and, to a lesser extent, birch leaves.
21 Greater concentrations of metal were observed in these species compared to cypress and
22 maple possibly due to differences in plant morphology and leaf surfaces. Solubility appeared
23 to be linked to the size fraction and, therefore, origin of the metal with those present
24 predominantly in the coarse fraction exhibiting low solubility.

25 **Capsule**

26 High density traffic resulted in elevated metal concentrations on vegetation, which were
27 related to distance from road and plant species.

28 **Keywords**

29 *Acer campestre*; *Betula pubescens*; *Chamaecyparis lawsonia*; Greenspace; *Urtica dioica*

30 **1 Introduction**

31 Particulate matter (PM) within the urban environment contains a range of metals that
32 are attributed to a number of both natural and anthropogenic sources (Harrison et al., 2003).
33 The metals Ba, Cd, Cr, Cu, Fe, Ni, Pb and Zn are often associated with high traffic densities;
34 originating from exhaust emission, tyre, brake, vehicle and engine wear, or the re-suspension
35 of road dusts (Allen et al., 2001; Harrison et al., 2003; Monaci et al., 2000; Riga-Karandinos
36 and Saitanis, 2004; Wählín et al., 2006).

37 Metals can be deposited onto vegetation growing in urban greenspaces as particles
38 or within rain or fog droplets, often referred to as dry, wet and occult deposition respectively.
39 Deposition of metals can be significant enough to cause short-term variations in foliar metal
40 concentration (Fernández Espinosa and Rossini Oliva, 2006; Kozlov et al., 1995; Monaci et
41 al., 2000; Riga-Karandinos and Saitanis, 2004) and can account for a large proportion of
42 metals recorded in plant leaves (Kozlov et al., 2000a; Riga-Karandinos and Saitanis, 2004).
43 Once deposited on vegetation, metals may be subject to diffusion across the cuticle or
44 stomata or accumulate on the leaf surfaces.

45 The role of urban trees in improving air quality has been given increasing attention in
46 recent years due to their relatively high capturing efficiencies compared with other types of
47 vegetation and land use (Bealey et al., 2006; Beckett et al., 2000a). However, in order to fully
48 assess the effect of urban air pollutants on plants, there is a need to quantify the rate of metal
49 deposition to urban species and the potential for plants to accumulate ecologically significant
50 amounts of metals. Above a certain concentration, most metals result in harm to the
51 vegetation itself (Grantz et al., 2003) and may present a risk to the wider ecosystem if
52 contaminated foliage is consumed and transferred through the food-chain (Notten et al., 2005;
53 Notten et al., 2006).

54 This study aims to quantify aerial deposition of metals to leaves by growing species
55 commonly planted in UK urban greenspaces in the urban roadside environment. The
56 variation in deposition between distance from road, plant species and metal will be discussed.
57 In addition, the soluble and insoluble fraction of metals within the plant tissue is presented to
58 provide an indication of their bioavailability to primary consumers.

59 **2 Materials and methods**

60 2.1 *Study sites*

61 *Park Square Gardens, Central London. National Grid Reference TQ286822, 0° 08.8' W, 51°*
62 *31.4' N.*

63 This is a city centre park maintained privately for the Crown Estate since the early
64 19th century. The park vegetation cover consists of lawn areas, small trees and shrubs and a
65 small amount of large trees including London plane (*Platanus x hispanica* Muenchh.) and
66 horse chestnut (*Aesculus hippocastanum* L.). In a survey carried out in 1988 by the London
67 Natural History Society it was identified as having one of the highest bird populations of small
68 open spaces in inner London (Baker, 1988). Marylebone Road, an often congested section of
69 the inner ring road of London, runs along the southern edge of the park. Marylebone Road is
70 a pollution 'hotspot' where air quality objectives for PM₁₀ are frequently exceeded (Fuller and
71 Green, 2006).

72 *Brompton Square, Central London. National Grid Reference TQ272792. 0° 10.0' W, 51° 29.8'*
73 *N.*

74 This garden is privately owned and maintained by the residents of Brompton Square
75 which was developed in the early 19th century. The soil is planted with a lawn, small trees,
76 shrubs, large ornamental trees and several large London plane and horse chestnut trees.
77 The garden is long and narrow, with a major arterial road, the A4, at the southern end and
78 terraced houses and a small road enclosing all other sides of the garden. PM₁₀
79 concentrations recorded at a nearby roadside sampler frequently exceed UK air quality
80 objectives (Fuller and Green, 2006).

81 *Alice Holt Research Station, Farnham, Surrey. National Grid Reference SU803428. 0° 51.1'*
82 *W, 51° 10.7' N.*

83 Additional plants were kept at a rural site away from major roads or PM₁₀ sources.
84 These plants were used as a control to relate measured metal concentrations to a
85 background range.

86 2.2 *Particulate matter and soil metal concentrations*

87 The concentration of airborne particulate matter adjacent to roads is substantially
88 higher than background levels (Harrison et al., 2004). Particulate and soil metal

89 concentrations were measured at each site to estimate the length and slope of any pollution
90 gradient. This information was used to determine the optimum positions for the plants to
91 represent the greatest decline in concentrations away from the road. Prior to the 19th century
92 both sites were outside the main city of London and likely to be used for agriculture, forestry
93 or, in the case of Marylebone Road, as royal hunting grounds. It is therefore assumed that a
94 survey of soil metals would be representative of historical air pollution rather than previous
95 land use. The transects were surveyed for total soil metal concentrations using field-portable
96 X-ray Fluorescence (FPXRF), which allows quick and reliable in situ measurements of metals
97 in the soil surface layer (Kilbride et al., 2006). The soil was analysed ten times at five
98 sampling locations (at 1, 5, 10, 25 and 55 m to the north of Marylebone Road and 1, 7, 12, 25,
99 and 50 m to the north of the A4). At each location any litter or grass was removed and the
100 soil compacted to provide a smooth, even surface. A reading was taken from each point by
101 pressing the FPXRF sampling window to the soil surface and depressing the trigger for 120
102 nominal seconds (Kilbride et al., 2006).

103 In order to confirm that soil metal concentrations are a result of contemporary as well
104 as historical deposition, a 12-hour daytime PM₁₀ concentration along the same transect was
105 measured on a day when the prevailing wind direction was from the road. The PM₁₀
106 concentration was sampled at the same five sampling locations as the soil metal levels with
107 three samplers operating at each point. The samplers used were the Sioutas cascade
108 impactor (SKC Ltd, UK), configured to collect PM₁₀ as three fractions (< 1 µm, 1-2.5 µm and
109 2.5-10 µm), with SKC Leyland Legacy sampling pumps. The pumps and filter-loaded
110 impactors were calibrated and set to run at a flow rate of 9 L min⁻¹. Sampling took place
111 during the day between 08:00 and 20:00. Gravimetric analysis of filters was carried out by a
112 commercial laboratory (Bureau Veritas, UK) according to the European Standard for
113 determination of the PM₁₀ fraction of suspended particulate matter (Standard Number
114 EN12341, 1999).

115 The soil and air sampling indicated that concentrations of PM₁₀ and metals generally
116 decreased with distance from the road (Table 1). The soil data suggested that the extent to
117 which distance from the road was a factor varied between metal and site, however the decline
118 in metal concentration was generally sharper within 10-12 m of the road and more gradual

119 between 12 and 50 m. PM₁₀ concentrations in the air were augmented within approximately
120 25 m of the road at both sites. A transect with a length of 12 m was therefore selected for
121 both sites to achieve a range of PM₁₀ exposure.

122 2.3 *Species selection*

123 Plant species used in this study were chosen to represent a large range of potential
124 particulate uptake rates and consideration was made of their prevalence in urban areas.
125 Field maple (*Acer campestre* L.) is very common in urban environments and its large, smooth
126 leaves result in relatively low particulate capture (Freer-Smith et al., 2005), in addition the
127 thick, waxy cuticle on the leaves is likely to restrict the absorption of soluble metals adhering
128 to leaf surfaces. Downy birch (*Betula pubescens* L.) is commonly found on roadside verges
129 and provides an importance habitat for herbivores; the leaves are small and downy and,
130 therefore, have the potential to be efficient particulate scavengers. Lawson cypress
131 (*Chamaecyparis lawsonia* (A. Murray) Parl.) is very common in urban areas, primarily due to
132 its use as a screen around private gardens. This species has very dense foliage and this,
133 combined with the fact that it is in-leaf throughout the year, results in a very high particulate
134 capturing efficiency (Beckett et al., 2000a; Freer-Smith et al., 2005). Common nettle (*Urtica*
135 *dioica* L.) is a common species in disturbed and derelict environments and is important for a
136 large number of invertebrate species, the leaves of which are covered with a great number of
137 fine hairs suggesting a potential for high particulate capture rates.

138 2.4 *Particulate deposition to plants*

139 Every care was taken to select trees from a relatively unpolluted nursery so that metal
140 concentrations in plants at the beginning of the experiment were representative of
141 background concentrations. Bare-rooted tree standards (1.5 to 1.8 m; age 1+2) were
142 obtained from a rural nursery (Prees Heath Forest Nursery, Shropshire, UK). Trees were
143 transferred to pots containing an uncontaminated peat-perlite mix. Stinging nettles were
144 grown from seed in the peat-perlite mix and were moved to site when their height had
145 reached approximately 20 cm. A transect length of 12 m was selected based on the results of
146 the soil and PM₁₀ data (Table 1), and plants were positioned in a completely randomised
147 design with three replicates of each species at 0, 2, 4, 6 and 12 m to the north of each road.

148 Plants were removed from their respective positions after 74 days at Brompton Square and
149 114 days at Alice Holt and Park Square Gardens.

150 Plants were harvested prior to leaf senescence. Leaves with petioles intact were
151 stripped from the branches. The leaves of cypress are scale-like and grow around woody
152 parts of the tree, making dissection of leaves from branches very difficult. Therefore, a
153 method to distinguish leaves from branches was used (Freer-Smith et al., 2005). This
154 method treats smooth barked sections as branches and irregularly shaped green sections as
155 leaves. The leaves were oven-dried at 70 °C overnight. The foliage was divided into two
156 sub-samples in order to quantify the total, water-soluble and insoluble metal fractions within
157 the leaves. The total metal concentrations were determined from the oven-dried samples.
158 The water-soluble and insoluble fractions were determined using the method outlined in
159 Kozlov et al. (2000a). The leaves were boiled in deionised water for 15 minutes, which aims
160 to remove approximately 90 % of the soluble metals from the leaf. The leaf material then was
161 oven-dried at 70 °C for 48 hours. The boiled leaves were assumed to contain insoluble
162 metals and a small fraction of soluble metals (< 10 %) not extracted by boiling (Kozlov et al.,
163 2000a).

164 Plant samples were dry-ashed at 450 °C for 18 hours and then wet digested
165 (Chapman, 1967). Wet digestion was achieved by incubating each sample for 1 hour at 60
166 °C in 0.75 cm³ concentrated ultra-pure HNO₃, followed by a further 14 hour incubation with
167 2.25 cm³ concentrated HCl and heating for 2 hours at 110 °C. After cooling, 0.15 cm³ of 30 %
168 H₂O₂ was added to each sample followed by heating for 30 minutes at 110 °C. To ensure
169 complete oxidation of all organic matter the H₂O₂ treatment was performed twice. The
170 digested samples were analysed for Ba, Cd, Cr Cu, Fe, Ni, Pb and Zn with a Spectro Flame
171 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES; Spectro Analytical
172 Instruments, West Midlands, UK) (Kilbride et al., 2006).

173 The solution resulting from the leaf boiling was centrifuged at 12 000 rpm for 15
174 minutes to remove any insoluble metal particles that may have been washed from fused sub-
175 cuticular waxes (Kozlov et al., 2000a). Organic precipitates in the solution were dissolved by
176 adding 1 ml hydrogen peroxide followed by UV digestion for 60 minutes at 80 °C. Further
177 additions of hydrogen peroxide were added until solutions were clear. Soluble metals were

178 determined by Spectro Flame Inductively Coupled Plasma – Optical Emission Spectrometer
179 (ICP-OES; Spectro Analytical Instruments, West Midlands, UK). Concentrations of soluble
180 metals in the leaf solvent were calculated in relation to dry mass of the leaves boiled.

181 2.5 *Statistical analysis*

182 Total Pb concentrations in the nettle tissue at the 2 m and 12 m distances from the
183 road at the Brompton Square site were omitted from the analysis due to inconsistencies
184 between the results. The total and soluble metal concentrations in the foliar tissues were
185 subjected to a log transformation to achieve an approximately normal distribution and jointly
186 analysed at the plot level using the REML algorithm in Genstat version 10.1 (Genstat, 2007).
187 The model included a general variance-covariance structure for the metals with independent
188 errors for site, species and distance from the road. Correlated errors for distance from the
189 road were considered, but were found not to be required. The model terms were tested using
190 a Wald test giving an *F*-statistic with approximate degrees of freedom. Residual plots were
191 examined to confirm model adequacy. Due to the large number of tests carried out a
192 protection level of α/k was used, where α is the chosen significance level (5%) and k is the
193 number of tests being considered.

194 The mean (across all distances) total and soluble foliar concentrations were
195 compared with the mean concentrations from the rural control site using an approximate t-test
196 with unequal variances and adjusted degrees of freedom (Winer, 1970) in Genstat version
197 10.1 (Genstat, 2007).

198 **3 Results**

199 3.1 *Total metal concentrations in the plant leaves*

200 The REML analysis found that there was no significant difference between the leaf
201 metal concentrations at the two sites. Unsurprisingly, the metal, plant species, distance from
202 the road and the interactions between them all had a significant affect on the leaf
203 concentrations (all $P < 0.001$). Individual metal concentrations were positively correlated with
204 one another (Table 2), relationships between Cd and Fe and Cr, Cu, Fe and Ni were
205 particularly strong ($r^2 > 0.87$). Considering all metals together, distance from the road had a
206 significant affect on leaf concentrations in birch ($P = 0.017$) and nettle ($P = 0.004$), but the

207 interaction between distance and metal was significant for birch ($P < 0.001$) and maple
208 ($P < 0.001$) leaf concentrations. However, separating the metals in the analysis showed that
209 distance away from the road only had a significant affect on the concentrations of Cu in birch
210 and maple leaves (Table 3; Figure 1), although concentrations of Cr, Fe and Ni in birch leaves
211 were approaching significance. Whereas Cd, Cr, Cu, Fe, Ni and Zn concentrations in nettle
212 leaves were all significantly affected by the distance from the road (Table 3; Figure 1). Metal
213 concentrations in the leaves of Lawson cypress were not significantly related to the distance
214 of the plants from the road.

215 Birch leaves grown at the London Parks had significantly greater concentrations of
216 Cd, Cr, Cu and Fe (all $P < 0.001$) compared with those grown at the rural control site (Table 4;
217 Figure 1). This was only true for Cu and Fe in the needles of Lawson Cypress (both
218 $P < 0.001$). Maple and nettle leaves had significantly greater concentrations of Cr, Fe, Ni, Zn
219 (all $P < 0.001$) and Cu ($P = 0.003$ and $P < 0.001$ respectively) when grown in the urban compared
220 with rural locations. Pb concentrations were not included in the statistical analysis due to all
221 but two of the values at the control site being zero. The maximum value was only 0.40 mg/kg.
222 The Pb concentrations at both Brompton Square and Park Square Gardens were all clearly
223 significantly greater than zero.

224 The ranking between species was consistent between the metals with birch and
225 nettle leaves having the greatest concentrations of all metals compared with both cypress and
226 maple (Table 3). Considering all metals together, there was no significant difference between
227 the concentrations in these two species, although, when taken individually, the Ba
228 concentrations in birch were significantly greater ($P = 0.024$) and the nettle concentrations
229 were significantly greater in the case of Cr ($P = 0.008$), Cu ($P = 0.018$), Fe ($P = 0.025$), Ni
230 ($P = 0.007$). Birch leaves had significantly greater concentrations of all metals compared with
231 cypress (all $P < 0.001$ except Ni where $P = 0.007$). Similarly, nettle concentrations were
232 significantly greater than cypress (all $P < 0.001$ except Pb where $P = 0.024$ and Zn where
233 $P = 0.025$). Birch Ba, Cd and Zn concentrations were significantly greater than those found in
234 maple ($P < 0.001$, $P = 0.025$ and $P < 0.001$ respectively), whereas nettle concentrations were
235 significantly greater for all metals (all $P < 0.001$ except Cd where $P = 0.004$ and Fe where
236 $P = 0.005$), with the exception of Pb. Maple leaves had significantly greater concentrations of

237 Cd (P=0.002), Cr (P=0.012), Cu (P<0.001), Fe (P<0.001) and Pb (P=0.016) than those found
238 in cypress needles.

239 The ranking between metal concentrations was consistent between species
240 (P<0.001; Table 3) and in the order Fe>Zn>Ba>Cu>Pb>Cr>Ni>Cd with all differences being
241 significant (all P<0.001).

242 3.2 Soluble metal concentrations in the plant leaves

243 Analysis of the data for the soluble metal concentrations in the leaves showed that
244 there was no significant affect of distance (Figure 2). However, there was a significant affect
245 of site (P=0.007), metal, species and their interactions (all P<0.001; Table 5; Figure 2).

246 Soluble concentrations of Cr, Cu and Pb were significantly greater in birch leaves
247 grown in Brompton Square (all P<0.001) and Park Square Gardens sites (all P<0.001)
248 compared with those from the rural control site (Table 5). Soluble Ni concentrations in birch
249 leaves from Brompton Square were also elevated (P<0.001). There was no significant
250 difference between the soluble metal concentrations in cypress leaves at either Brompton
251 Square or Park Square Gardens compared with the rural control site.

252 Generally, there were no significant differences between the two sites when
253 comparing the mean concentrations for each species, the only exceptions being that the birch
254 trees grown at Brompton Square had significantly greater Cd and Cr concentrations
255 compared with those from Park Square Gardens (Table 5; both P<0.001). The dataset was
256 unbalanced due the missing Cd and Cr values for maple, and therefore the analysis was
257 repeated omitting these results. As with the total metal concentrations, birch had the greatest
258 concentrations of soluble metal concentrations compared with the cypress and maple,
259 although for cypress this was only significant for Ba, Cu, Ni and Zn (all P<0.001) and for Ba
260 was only significant for Ba, Fe, Ni, Pb and Zn (all P<0.001). There was generally no
261 significant difference between the soluble metal concentrations in the leaves of Lawson
262 cypress and maple, with the exception of Cu where concentrations in maple were greater
263 than those in cypress (P<0.001).

264 The ranking between metal concentrations was, again consistent between species
265 (P<0.001; Table 5) and in the order Zn>Fe>Ba>Cu>Pb, Ni>Cr>Cd, with all differences being
266 significant (P<0.001) with the exception of Pb and Ni. The comparison between Cd and Cr

267 applies to birch and cypress only. This order generally follows a similar pattern to that for
268 total metals, except that Zn concentrations are greater than Fe and Ni concentrations are
269 greater than Cr, suggesting a greater portion of Zn and Ni are in soluble forms.

270 **4 Discussion**

271 *4.1 Effect of vehicle emissions on metal concentration in plant leaves*

272 Brompton Square and Park Square Gardens were selected for this study as they are
273 close to roads that are recognised particulate 'hotspots' where air quality objectives are often
274 breached due to the high traffic densities (Fuller and Green, 2006). Downy birch, Lawson
275 cypress, field maple and common nettle, all grown in a transect away from these roads, had
276 elevated concentrations of Cd, Cr, Cu, Fe, Ni, Pb and/or Zn in their leaves compared to those
277 grown in the rural control site. All of these metals are associated with particulate pollution
278 originating from roads, suggesting that the high traffic densities are resulting in an increased
279 metal load to nearby vegetation. Other studies have also reported significantly elevated
280 concentrations of Cd, Cu, Fe, Ni, Pb and Zn in trees grown in roadside environments
281 (Fernández Espinosa and Rossini Oliva, 2006; Monaci et al., 2000).

282 The mean concentrations reported here are all within similar ranges to those found in
283 previous studies using different species (Fernández Espinosa and Rossini Oliva, 2006;
284 Monaci et al., 2000; Riga-Karandinos and Saitanis, 2004), although there is some variation.
285 For example, the Ba, Cu, Fe, Ni, and Pb concentrations reported by Fernández Espinosa and
286 Rossini Oliva (2006) on the leaves of oleander and lantana grown in Seville, Spain are often
287 lower than those reported here, which is probably mainly due to the lower traffic densities;
288 23067 vehicles per day compared with the 71200 vehicles per day recorded on Marylebone
289 Road (Department for Transport, 2002). Whereas the Pb concentrations are smaller than
290 those found by Monaci et al. (2000) in the leaves of evergreen oak presumably because their
291 study pre-dated the phasing out of leaded fuel.

292 Metal deposition has been correlated with tree mortality and injury in rural areas
293 (Gawel et al., 1996) and toxicity at the ecosystem level has been related to soil microbial
294 activity rather than direct effects on the plants (Grantz et al., 2003). The likely physiological
295 effects of airborne metal deposition are difficult to gauge for plants as the majority of toxicity
296 experiments relate toxic effects to root uptake rather than their deposition as particles to leaf

297 surfaces. The concentrations of metals in tree foliage, as a result of root uptake, reported to
298 have a toxicological effect are generally much greater than the concentrations in the present
299 study (Smith and Brennan, 1984; Heale and Omrod, 1982; Carlson and Bazzaz, 1977; Brown
300 and Wilkins, 1985). This suggests that despite the elevated concentrations compared to the
301 control site they are unlikely to result in any direct toxicity to the plant species studied.

302 There were no major differences between leaf metal concentrations at Brompton
303 Square and at Park Square Gardens where plants were exposed for 55% longer. This
304 suggests that adsorption sites on the leaf may be quickly filled with metal particles so that
305 after a short exposure period (<11 weeks) the metal concentrations plateau. This hypothesis
306 is supported by evidence from leaf washing studies which have shown that a portion (more
307 than 65%) of metal is retained permanently on the leaf surface (Kozlov et al., 2000a).
308 Moreover, a previous study of metal burdens over the entire season showed that metal
309 concentrations either remained constant throughout the season or increased during the first
310 half of the growing season and decreased during the latter half (Smith and Staskawicz, 1977).
311 Another explanation for the similarity in foliar metal concentrations between sites is that the
312 average deposition rate was higher at Brompton Square or that there were differences in the
313 dispersion of the particulates over the parks.

314 Despite these elevated concentrations and the observed decline in PM₁₀
315 concentrations within 12 m from each road, distance from the road did not have a consistent
316 affect on metal concentrations in the leaf tissue from the three tree species investigated. Only
317 Cu concentrations in birch and maple leaves were significantly related to the distance from
318 the road. The affect of distance was, however, closely related to the total concentrations of
319 Cd, Cr, Cu, Fe, Ni and Zn in the nettle leaves.

320 *4.2 Differences in metal concentration between plant species*

321 The difference in metal concentrations between species is likely to be due to
322 differences in their leaf arrangement, morphology and/or surface properties. Species with a
323 large number of small, hairy and sticky leaves have been shown to exhibit high particulate
324 capturing efficiencies (Beckett et al., 2000a; Freer-Smith et al., 2004; Freer-Smith et al.,
325 2005). Nettle and birch leaves exhibit these characteristics explaining the greater
326 concentrations observed in the leaves of these species compared with the cypress and

327 maple. Although only Cu concentrations in birch were significantly affected by distance from
328 the road, Cr, Fe and Ni concentrations did appear to be declining. This, together with the fact
329 that metal concentrations in nettle were often greater than those in birch, suggests that if the
330 exposure period had been extended the differences in concentration in birch along the
331 transect may have become more pronounced. The affect of distance on nettle concentrations
332 may have been a function of the smaller height of this species compared with the trees
333 (Smith, 1976). The tree species used in this study were all standards, with heights of
334 between 1.5 to 1.8 m, whereas the nettle plants were positioned on site when their heights
335 were 0.2 m. The nettles are therefore more likely to be exposed to re-suspended road dusts
336 (Fernández Espinosa and Rossini Oliva, 2006) and spray from roads during wet weather than
337 the taller tree species. This is supported by the dramatic decline between the 0 and 2 m
338 distances observed in the nettle tissue concentrations at Park Square Gardens.

339 The relatively low metal concentration in maple leaves is likely to be due to their
340 comparatively large leaves and waxy cuticles (Pyatt, 1973). Cypress has previously been
341 reported to have a greater particulate capturing efficiency than other tree species due to their
342 dense needle structure (Beckett et al., 2000b), but in this study the needle metal
343 concentrations were smaller compared with the other species. The greater capturing
344 efficiencies are based on the mass of particles deposited on the plant as a whole and, as
345 cypress has a large leaf area index and therefore surface area, the total mass of particulates
346 may be large, despite the concentration per mass of foliage being low. Unlike the other tree
347 species tested, which lose their leaves each year, cypress needles may be retained for 2-10
348 years so the concentrations of metals within them may accumulate to significantly greater
349 levels than those reported here or those found in deciduous species.

350 4.3 *Differences in plant leaf concentrations between metals*

351 Leaf concentrations of the eight metals were all positively correlated with each other,
352 suggesting that all metals originate from the same source/s (Monaci et al., 2000). Previous
353 studies have also found that metal concentrations in plant tissues exposed to traffic sources
354 are correlated (Monaci et al., 2000; Riga-Karandinos and Saitanis (2004). Here the
355 correlations between Cd and Fe and Cr, Cu, Fe and Ni were particularly strong and this is
356 likely to represent their particular origins within the overall traffic source. Anthropogenic Fe,

357 Cr and Cu originate primarily from brake wear (Harrison et al., 2003; Monaci et al., 2000;
358 Tasdemir et al., 2005; Wählén et al., 2006) and other studies have shown strong correlations
359 between the concentrations of these metals on the surfaces of leaves (Monaci et al., 2000;
360 Riga-Karandinos and Saitanis, 2004). Cd is present in the products of tyre wear and exhaust
361 emissions (Allen et al., 2001; Monaci et al., 2000), the strong relationship between this metal
362 and Cu cannot be explained specifically, as, although they are both present in exhaust
363 emissions, this is also true of several other metals for which the correlations are much weaker
364 (Allen et al., 2001). Harrison et al. (2003), however, found that the size distribution of Cd
365 within particles suggested that it originated primarily from wear rather than combustion which
366 may explain its correlation with Cu. Fe is a crustal metal (Monaci et al., 2000; Tasdemir et al.,
367 2005) and the greater concentrations of this compared to the anthropogenic metals suggests
368 than soil dusts have been re-suspended by tyre shear (Tasdemir et al., 2005). Leaf metal
369 concentrations followed the order Fe>Zn>Ba>Cu>Pb>Cr>Ni>Cd for total concentrations and
370 Zn>Fe>Ba>Cu>Pb, Ni>Cr>Cd for soluble metals. This ordering is similar to that found in
371 other studies investigating the composition of PM₁₀ (Allen et al., 2001; Tasdemir et al., 2005),
372 suggesting that the particulate pollution in London is representative of a 'typical' composition.

373 Total concentrations of Fe were around 5 times greater than those for Zn, whereas
374 soluble concentrations of Zn were around 1.5 times those of Fe. Similarly, total
375 concentrations of Cr were around double those of Ni, whereas soluble concentrations of Ni
376 were around 4 times those of Cr. Their reversal of positions in the ranking of concentrations
377 suggests that significant proportions of the Zn and Ni are in a soluble form (approximately
378 10% and 13% respectively) compared to a very small proportion of Fe and Cr (approximately
379 1%). Fe and Cr are primarily present within the coarse (PM_{2.5-10}) fraction, whereas Zn and Ni
380 have an even size distribution indicative of a range of sources which may explain why a
381 greater proportion of these metals is in a soluble form (Harrison et al., 2003). Soluble metal
382 fractions were generally lower than fractions measured in the air by other workers. For
383 example, solubility of Cd, Cu, Pb and Zn in atmospheric aerosol has been reported to range
384 from 25-90%, 27-90%, 4-70% and 73-93% respectively (Hoffmann et al. 1997; Fernandez et
385 al. 2002; Voutsas and Samara 2002). It is very difficult to draw conclusions about the relative
386 amount of water-soluble trace metals in particulate matter because it depends on relative

387 contributions of various emission sources to ambient particulate matter and meteorological
388 conditions, both of which vary over time (Tomasevic et al., 2005). Assuming the soluble
389 fraction of metals deposited to trees during the present study were similar to those cited in the
390 literature, then it is evident here that a loss of soluble metal has occurred at some point, most
391 likely through leaf runoff following precipitation which removes water-soluble deposits more
392 rapidly than insoluble deposits (Rodrigo and Avila, 2002). However, the domination of
393 insoluble metals in leaf particulate deposits may also suggest the main components of the
394 particles are derived from road dusts and soil re-suspension (Duan et al., 2005; Manalis et al.,
395 2005). In stable atmospheric conditions, coarse particles, such as these, will deposit very
396 quickly (QUARG, 1996). This is supported by the rapid fall of metal levels away from the
397 road, which is characteristic of coarse particle dispersion (QUARG, 1996).

398 **5 Conclusion**

399 This study provides further evidence that traffic represents a significant source of
400 metal contamination to urban vegetation, particularly that growing in the immediate vicinity of
401 the road. Plant species plays a significant role in the metal concentration in leaf tissue which
402 may be due to differences in leaf arrangement, morphology, surface characteristics and the
403 height of vegetation. Despite this atmospheric deposition of metals to plant surfaces of the
404 species tested here is unlikely to result in a significant immediate risk of direct toxicity to the
405 plant or primary consumers. The results suggest that the risk of creating new pathways for
406 metal contamination from deposition of particulate matter to ecological receptors through
407 greenspace establishment in roadside environments is relatively low.

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416

417 **6 References**

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531 **Fig. 1.** Total a) Ba, b) Cd, c) Cr, d) Cu, e) Fe, f) Ni, g) Pb and h) Zn concentrations in the foliar
532 tissue from downy birch, Lawson cypress, field maple and common nettles planted at varying
533 distances from two heavily polluted London roads in Brompton Square (74 days; black
534 squares, dashed lines) and Park Square Gardens (114 days; crosses solid lines) and a rural
535 control site (114 days; open circles).
536

537 **Fig. 2.** Soluble a) Ba, b) Cd, c) Cr, d) Cu, e) Fe, f) Ni, g) Pb and h) Zn concentrations in the
538 foliar tissue from downy birch, Lawson cypress and field maples planted at varying distances
539 from two heavily polluted London roads in Brompton Square (74 days; black squares, dashed
540 lines) and Park Square Gardens (114 days; crosses solid lines) and a rural control site (114
541 days; open circles).

542 **Table 1**
 543 Mean soil metal and PM₁₀ concentrations (mg/kg and µg/m³) at Park Square Gardens and Brompton Square.

	n	Distance from roadside (m)				
Brompton Square		1	7	12	25	50
Cu (mg/kg)	50	80.8 (±4.8)	77.1 (±1.3)	78.8(±1.9)	70.0 (±1.8)	54.5 (±1.3)
Fe (mg/kg)	50	1266 (±89.0)	1071 (±23.3)	1198 (±42.0)	996 (±22.2)	783 (±21.2)
Mn (mg/kg)	50	17.9 (± 1.0)	17.9 (±0.7)	20.2 (±1.9)	15.5 (±0.9)	13.8 (±0.6)
Ni (mg/kg)	50	13.7 (± 0.8)	13.8 (±0.8)	14.8 (±0.9)	13.1 (±0.7)	9.4 (±0.6)
Pb (mg/kg)	50	151.9 (±14.4)	96.5 (±6.0)	97.6 (±5.1)	117.5 (±3.2)	66.7 (±4.5)
Zn (mg/kg)	50	117.1 (±19.4)	84.5 (±3.8)	76.3 (±3.1)	67.0 (±1.5)	45.9 (±2.3)
PM ₁₀ (µg/m ³)	11	70.4 (±24.1)	53.8 (±16.1)	58.8 (±19.4)	36.6 (±10.5)	44.0 (±6.9)
Park Square Gardens		1	5	10	25	55
Cu (mg/kg)	43	77.2 (±3.6)	90.0 (±1.8)	80.3 (±2.2)	80.2 (±4.9)	80.2 (±2.0)
Fe (mg/kg)	43	1237 (±104.4)	1613 (±25.5)	1637 (±22.1)	1156 (±81.1)	1299 (±31.8)
Mn (mg/kg)	43	20.2 (±1.5)	21.1 (±0.9)	21.7 (±0.6)	16.1 (±1.0)	17.7 (±1.0)
Ni (mg/kg)	43	12.6 (±1.3)	16.1 (±0.7)	15.9 (±1.4)	15.7 (±1.4)	12.1 (±0.7)
Pb (mg/kg)	43	159.1(±25.2)	162.3 (±9.8)	147.3 (±5.6)	84.0 (±8.0)	106.5 (±6.6)
Zn (mg/kg)	43	99.6 (±9.0)	88.7 (±3.9)	71.2 (±0.7)	96.4 (±9.3)	57.7 (±1.9)
PM ₁₀ (µg/m ³)	10	77.2 (±27.3)	30.7 (±9.0)	21.76 (±9.7)	14.6 (±8.3)	32.5 (±20.6)

544 Quality level for FPXRF data: Ni – qualitative; Cu, Mn, Zn quantitative; Pb, Fe definitive (Kilbride et al., 2006). Values in parenthesis represent the standard error of the mean.

545 **Table 2**

546 Correlation co-efficients between the metal concentrations measured in downy birch, Lawson
 547 cypress, field maple and common nettle following exposure to particulate pollution from two
 548 urban roads (n=48).

Correlation co-efficients between metal concentrations								
Ba	1.00							
Cd	0.74	1.00						
Cr	0.57	0.62	1.00					
Cu	0.69	0.70	0.96	1.00				
Fe	0.67	0.75	0.96	0.96	1.00			
Ni	0.56	0.60	0.93	0.88	0.87	1.00		
Pb	0.51	0.46	0.66	0.60	0.68	0.54	1.00	
Zn	0.60	0.40	0.44	0.45	0.43	0.53	0.60	1.00
	Ba	Cd	Cr	Cu	Fe	Ni	Pb	Zn

549 **Table 3**

550 Log metal concentrations in leaves of downy birch, Lawson cypress, field maple and common nettle exposed for up to 114 days to particulate emissions at
 551 varying distances (up to 12 m) from two heavily polluted London roads and the associated t-values for the effect of the distance of the plants from the roads.

Metal	Log metal concentrations (mg/kg)							
	Birch (n=15)		Cypress (n=14)		Maple (n=8)		Nettle (n=11)	
	Estimate ^a	t-value	Estimate ^a	t-value	Estimate ^a	t-value	Estimate ^a	t-value
Ba	-0.0146 (0.0196)	-0.745	-0.0166 (0.0196)	-0.846	-0.0105 (0.0202)	-0.518	-0.0154 (0.0196)	-0.785
Cd	-0.0040 (0.0159)	-0.254	-0.0086 (0.0159)	-0.543	0.0232 (0.0164)	1.414	-0.0648 (0.0159)	-4.067 ^b
Cr	-0.0401 (0.0161)	-2.482	-0.0154 (0.0161)	-0.952	-0.0194 (0.0166)	-1.169	-0.0843 (0.0162)	-5.213 ^b
Cu	-0.0585 (0.0155)	-3.775 ^b	-0.0230 (0.0155)	-1.482	-0.0429 (0.0160)	-2.689 ^b	-0.0864 (0.0155)	-5.565 ^b
Fe	-0.0314 (0.0154)	-2.040	-0.0199 (0.0154)	-1.295	-0.0230 (0.0159)	-1.448	-0.0759 (0.0154)	-4.922 ^b
Ni	-0.0297 (0.0139)	-2.135	-0.0061 (0.0139)	-0.441	-0.0079 (0.0143)	-0.553	-0.0970 (0.0139)	-6.958 ^b
Pb	-0.0273 (0.0427)	-0.640	-0.0122 (0.0427)	-0.287	0.0004 (0.0439)	0.008	-0.1109 (0.0470) ^c	-2.361
Zn	-0.0025 (0.0217)	-0.115	-0.0118 (0.0217)	-0.543	-0.0089 (0.0223)	-0.400	-0.1092 (0.0217)	-5.026 ^b

552 ^aEstimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; ^bDenotes significance, where P<0.0015; ^cn=5.

553 **Table 4**

554 Log differences in metal concentrations in leaves of downy birch, Lawson cypress, field maple and common nettle exposed for up to 114 days to particulate
 555 emissions from two heavily polluted London roads compared with those from a rural control site and the associated t-values for the effect urban versus rural
 556 locations.

Metal	Log differences in metal concentrations compared to the rural control site (mg/kg)							
	Birch (n=15)		Cypress (n=14)		Maple (n=8)		Nettle (n=11)	
	Estimate ^a	t-value	Estimate ^a	t-value	Estimate ^a	t-value	Estimate ^a	t-value
Ba	0.574 (0.269)	2.14	0.039 (0.158)	0.25	0.566 (0.232)	2.44	-0.257 (0.131)	-1.96
Cd	0.805 (0.107)	7.53 ^b	0.321 (0.144)	2.23	0.565 (0.417)	1.35	1.187 (0.339)	3.50
Cr	1.672 (0.170)	9.84 ^b	0.954 (0.178)	5.37	1.421 (0.167)	8.51 ^b	2.160 (0.195)	11.06 ^b
Cu	2.399 (0.169)	14.19 ^b	0.954 (0.126)	7.54 ^b	1.840 (0.208)	8.85	1.874 (0.126)	14.90 ^b
Fe	1.898 (0.138)	13.71 ^b	0.958 (0.103)	9.29 ^b	1.408 (0.170)	8.31 ^b	1.993 (0.125)	15.94 ^b
Ni	0.764 (0.423)	1.81	0.225 (0.131)	1.72	0.909 (0.104)	8.72 ^b	1.378 (0.123)	11.22 ^b
Zn	0.717 (0.212)	3.39	0.006 (0.143)	0.04	0.826 (0.191)	4.33 ^b	1.216 (0.179)	6.81*

557 ^aEstimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; ^bDenotes significance, where P<0.002

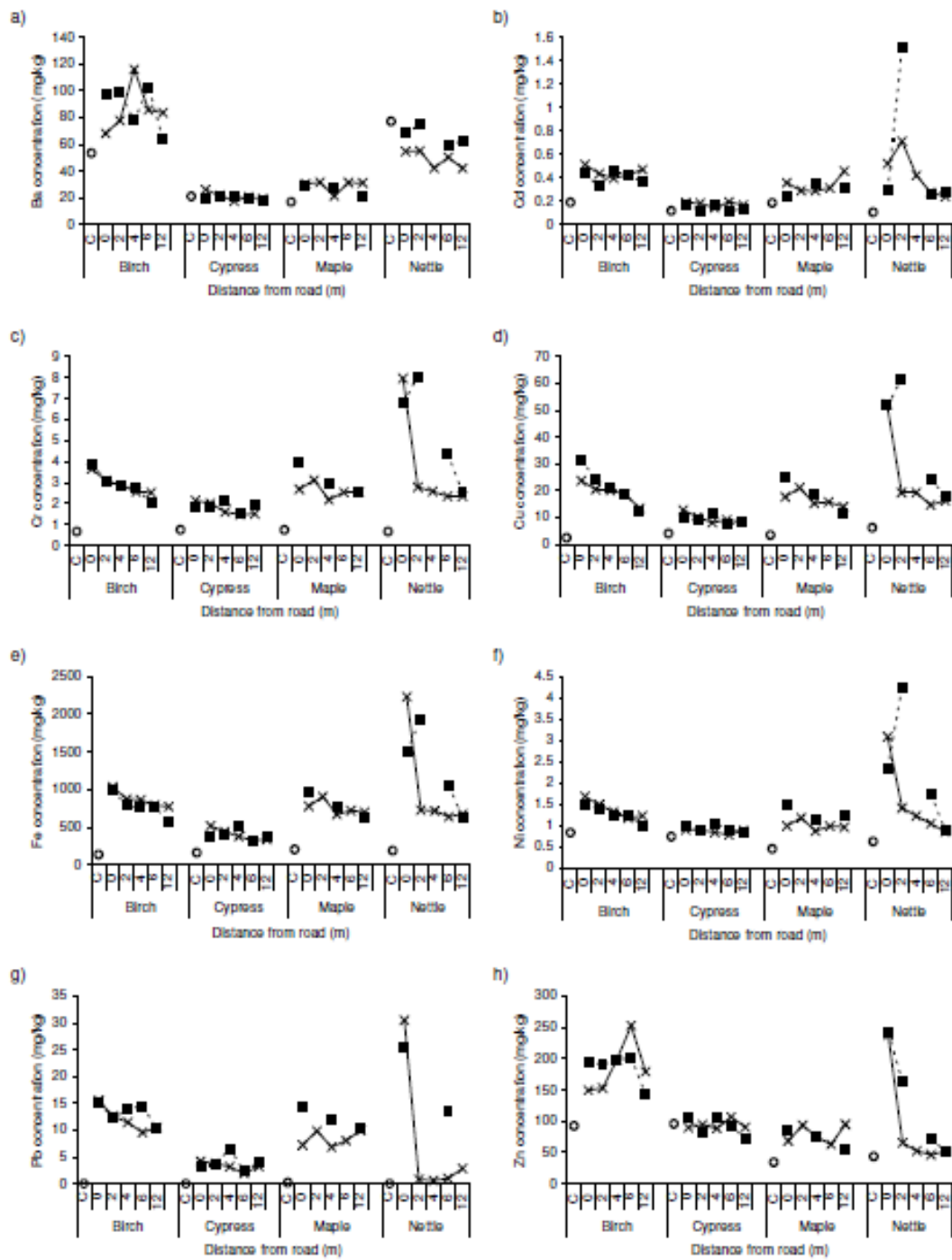
558 **Table 5**

559 Log soluble metal concentrations in leaves of downy birch, Lawson cypress and field maple exposed to particulate emissions at varying distances (up to 12
560 m) from two heavily polluted London roads at Brompton Square (74 day exposure) and Park Square Gardens (114 day exposure) and the differences
561 between these concentrations compared with those from a rural control site (114 day exposure) and the associated t-values for the effect urban versus rural
562 locations.

Site	Metal	Log soluble metal concentrations at the two London sites and the differences between those from the rural control site (mg/kg)								
		Birch (n=15)			Cypress (n=14)			Maple (n=8)		
		Estimate ^a	Difference	t-value	Estimate ^a	Difference	t-value	Estimate ^a	Difference	t-value
Brompton Square	Ba	1.944 (0.199)	0.36 (0.336)	1.08	0.306 (0.199)	-0.63 (0.213)	-2.98	0.674 (0.257)	0.24 (0.541)	0.44
	Cd	-3.355 (0.311)	0.19 (0.363)	0.51	-4.852 (0.343)	-0.15 (0.428)	-0.36			
	Cr	-2.381 (0.213)	1.03 (0.225)	4.56 ^b	-3.537 (0.213)	-0.03 (0.221)	-0.12			
	Cu	0.467 (0.228)	2.09 (0.252)	8.31 ^b	-1.386 (0.228)	0.59 (0.259)	2.29	0.458 (0.294)	1.38 (0.561)	2.45
	Fe	2.080 (0.230)	2.72 (0.692)	3.93	1.585 (0.230)	1.62 (0.433)	3.74	1.276 (0.296)	3.00 (0.392)	7.65 ^b
	Ni	-1.279 (0.153)	1.08 (0.195)	5.54 ^b	-2.384 (0.153)	-0.28 (0.193)	-1.44	-2.114 (0.198)	0.13 (0.285)	0.46
	Pb	-1.512 (0.181)	5.07 (0.339)	14.98 ^b	-2.342 (0.181)	2.27 (0.415)	5.47	-2.298 (0.233)	(0.240)	0.00
Park Square Gardens	Zn	2.976 (0.154)	0.30 (0.229)	1.29	1.897 (0.154)	-0.17 (0.214)	-0.78	1.873 (0.199)	0.06 (0.476)	0.12
	Ba	1.485 (0.199)	-0.09 (0.202)	-0.28	0.322 (0.199)	-0.62 (0.202)	-2.91	0.444 (0.199)	0.01 (0.202)	0.01
	Cd	-3.765 (0.656)	-0.33 (0.642)	-0.49	-5.705 (0.391)	-1.06 (0.382)	-2.28			
	Cr	-4.424 (0.229)	-1.02 (0.231)	-4.23 ^b	-3.803 (0.213)	-0.29 (0.214)	-1.32	-1.235 (0.405)	2.13 (0.404)	5.18 ^b
	Cu	0.625 (0.228)	2.25 (0.227)	8.93 ^b	-1.102 (0.228)	0.88 (0.227)	3.38	0.421 (0.228)	1.34 (0.227)	2.53
	Fe	2.433 (0.230)	3.07 (0.230)	4.44	1.876 (0.230)	1.91 (0.230)	4.41	1.524 (0.230)	3.25 (0.230)	9.43 ^b
	Ni	-1.706 (0.153)	0.66 (0.162)	3.35	-2.49 (0.153)	-0.38 (0.162)	-1.99	-2.621 (0.153)	-0.38 (0.162)	-1.49
Pb	-1.459 (0.181)	5.12 (0.186)	15.13 ^b	-1.922 (0.181)	2.69 (0.186)	6.49	-3.775 (0.196)			
Zn	2.995 (0.154)	0.32 (0.163)	1.38	2.151 (0.154)	0.09 (0.163)	0.41	1.790 (0.154)	-0.02 (0.163)	-0.05	

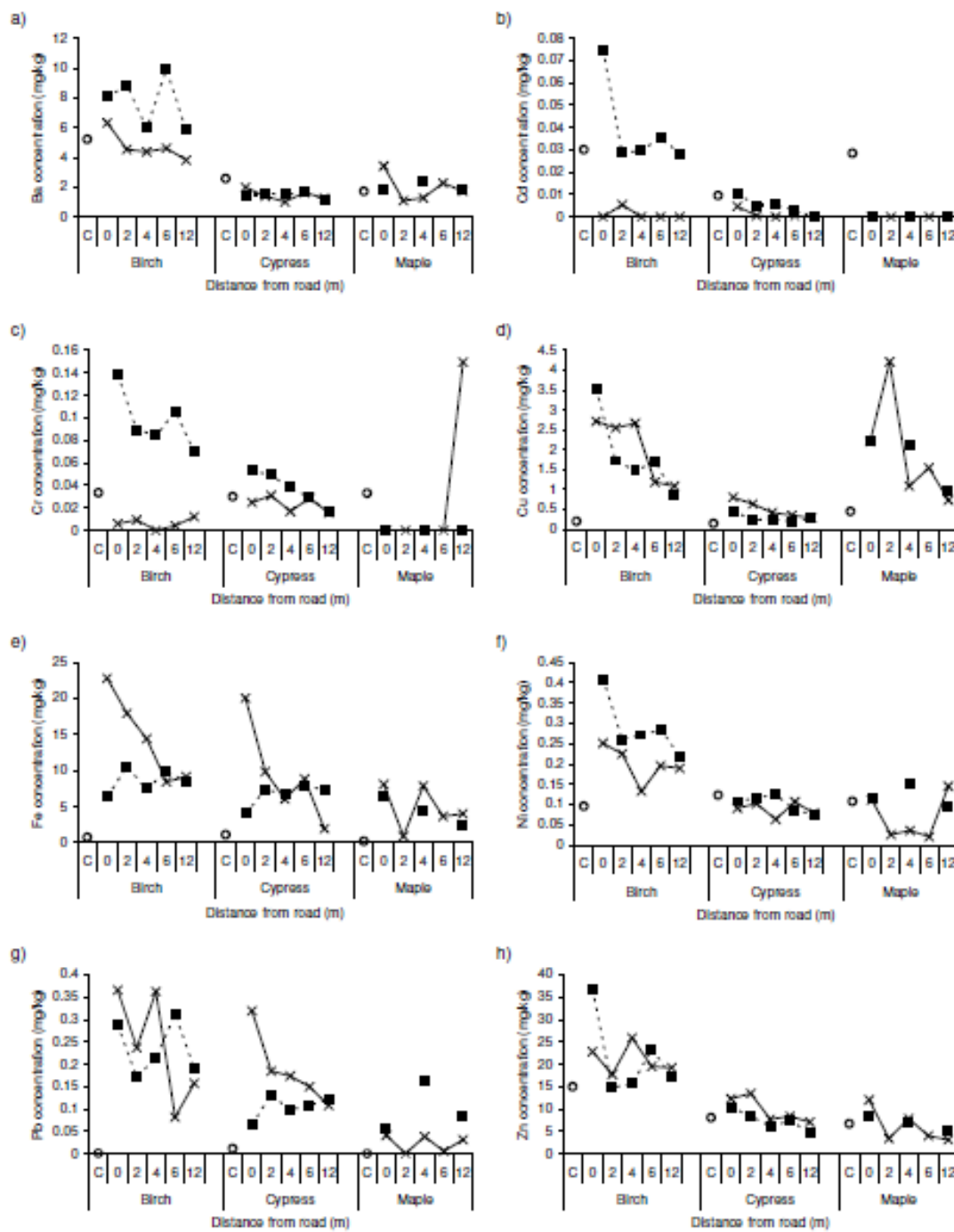
563 ^aEstimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; ^bDenotes significance, where P<0.001

564 Figure 1



565

566 Figure 2



567