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

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Abstract

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

Capsule

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

Keywords

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

1 Introduction

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

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

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

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

2 Materials and methods

2.1 Study sites

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

This is a city centre park maintained privately for the Crown Estate since the early 19th century. The park vegetation cover consists of lawn areas, small trees and shrubs and a small amount of large trees including London plane (*Platanus x hispanica* Muenchh.) and horse chestnut (*Aesculus hippocastanum* L.). In a survey carried out in 1988 by the London Natural History Society it was identified as having one of the highest bird populations of small open spaces in inner London (Baker, 1988). Marylebone Road, an often congested section of the inner ring road of London, runs along the southern edge of the park. Marylebone Road is a pollution 'hotspot' where air quality objectives for PM_{10} are frequently exceeded (Fuller and Green, 2006).

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

This garden is privately owned and maintained by the residents of Brompton Square which was developed in the early 19th century. The soil is planted with a lawn, small trees, shrubs, large ornamental trees and several large London plane and horse chestnut trees. The garden is long and narrow, with a major arterial road, the A4, at the southern end and terraced houses and a small road enclosing all other sides of the garden. PM_{10} concentrations recorded at a nearby roadside sampler frequently exceed UK air quality objectives (Fuller and Green, 2006).

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

Additional plants were kept at a rural site away from major roads or PM_{10} sources. These plants were used as a control to relate measured metal concentrations to a background range.

2.2 Particulate matter and soil metal concentrations

The concentration of airborne particulate matter adjacent to roads is substantially higher than background levels (Harrison et al., 2004). Particulate and soil metal concentrations were measured at each site to estimate the length and slope of any pollution gradient. This information was used to determine the optimum positions for the plants to represent the greatest decline in concentrations away from the road. Prior to the 19th century both sites were outside the main city of London and likely to be used for agriculture, forestry or, in the case of Marylebone Road, as royal hunting grounds. It is therefore assumed that a survey of soil metals would be representative of historical air pollution rather than previous land use. The transects were surveyed for total soil metal concentrations using field-portable X-ray Fluorescence (FPXRF), which allows quick and reliable in situ measurements of metals in the soil surface layer (Kilbride et al., 2006). The soil was analysed ten times at five sampling locations (at 1, 5, 10, 25 and 55 m to the north of Marylebone Road and 1, 7, 12, 25, and 50 m to the north of the A4). At each location any litter or grass was removed and the soil compacted to provide a smooth, even surface. A reading was taken from each point by pressing the FPXRF sampling window to the soil surface and depressing the trigger for 120 nominal seconds (Kilbride et al., 2006).

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

The soil and air sampling indicated that concentrations of PM_{10} and metals generally decreased with distance from the road (Table 1). The soil data suggested that the extent to which distance from the road was a factor varied between metal and site, however the decline in metal concentration was generally sharper within 10-12 m of the road and more gradual between 12 and 50 m. PM_{10} concentrations in the air were augmented within approximately 25 m of the road at both sites. A transect with a length of 12 m was therefore selected for both sites to achieve a range of PM_{10} exposure.

2.3 Species selection

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

2.4 Particulate deposition to plants

Every care was taken to select trees from a relatively unpolluted nursery so that metal concentrations in plants at the beginning of the experiment were representative of background concentrations. Bare-rooted tree standards (1.5 to 1.8 m; age 1+2) were obtained from a rural nursery (Prees Heath Forest Nursery, Shropshire, UK). Trees were transferred to pots containing an uncontaminated peat-perlite mix. Stinging nettles were grown from seed in the peat-perlite mix and were moved to site when their height had reached approximately 20 cm. A transect length of 12 m was selected based on the results of the soil and PM_{10} data (Table 1), and plants were positioned in a completely randomised design with three replicates of each species at 0, 2, 4, 6 and 12 m to the north of each road.

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

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

Plant samples were dry-ashed at 450 ^{o}C for 18 hours and then wet digested (Chapman, 1967). Wet digestion was achieved by incubating each sample for 1 hour at 60 ^{o}C in 0.75 cm^3 concentrated ultra-pure HNO_3, followed by a further 14 hour incubation with 2.25 cm^3 concentrated HCl and heating for 2 hours at 110 ^{o}C. After cooling, 0.15 cm^3 of 30 % H_2O_2 was added to each sample followed by heating for 30 minutes at 110 ^{o}C. To ensure complete oxidation of all organic matter the H_2O_2 treatment was performed twice. The digested samples were analysed for Ba, Cd, Cr Cu, Fe, Ni, Pb and Zn with a Spectro Flame Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES; Spectro Analytical Instruments, West Midlands, UK) (Kilbride et al., 2006).

The solution resulting from the leaf boiling was centrifuged at 12 000 rpm for 15 minutes to remove any insoluble metal particles that may have been washed from fused sub-cuticular waxes (Kozlov et al., 2000a). Organic precipitates in the solution were dissolved by adding 1 ml hydrogen peroxide followed by UV digestion for 60 minutes at 80 ^{o}C. Further additions of hydrogen peroxide were added until solutions were clear. Soluble metals were determined by Spectro Flame Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES; Spectro Analytical Instruments, West Midlands, UK). Concentrations of soluble metals in the leaf solvent were calculated in relation to dry mass of the leaves boiled.

2.5 Statistical analysis

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

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

3 Results

3.1 Total metal concentrations in the plant leaves

The REML analysis found that there was no significant difference between the leaf metal concentrations at the two sites. Unsurprisingly, the metal, plant species, distance from the road and the interactions between them all had a significant affect on the leaf concentrations (all $P<0.001$). Individual metal concentrations were positively correlated with one another (Table 2), relationships between Cd and Fe and Cr, Cu, Fe and Ni were particularly strong ($r^2>0.87$). Considering all metals together, distance from the road had a significant affect on leaf concentrations in birch ($P=0.017$) and nettle ($P=0.004$), but the interaction between distance and metal was significant for birch (P<0.001) and maple (P<0.001) leaf concentrations. However, separating the metals in the analysis showed that distance away from the road only had a significant affect on the concentrations of Cu in birch and maple leaves (Table 3; Figure 1), although concentrations of Cr, Fe and Ni in birch leaves were approaching significance. Whereas Cd, Cr, Cu, Fe, Ni and Zn concentrations in nettle leaves were all significantly affected by the distance from the road (Table 3; Figure 1). Metal concentrations in the leaves of Lawson cypress were not significantly related to the distance of the plants from the road.

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

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

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

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

3.2 Soluble metal concentrations in the plant leaves

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

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

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

The ranking between metal concentrations was, again consistent between species (P<0.001; Table 5) and in the order Zn>Fe>Ba>Cu>Pb, Ni>Cr>Cd, with all differences being significant (P<0.001) with the exception of Pb and Ni. The comparison between Cd and Cr applies to birch and cypress only. This order generally follows a similar pattern to that for total metals, except that Zn concentrations are greater than Fe and Ni concentrations are greater than Cr, suggesting a greater portion of Zn and Ni are in soluble forms.

4 Discussion

4.1 Effect of vehicle emissions on metal concentration in plant leaves

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

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

Metal deposition has been correlated with tree mortality and injury in rural areas (Gawel et al., 1996) and toxicity at the ecosystem level has been related to soil microbial activity rather than direct effects on the plants (Grantz et al., 2003). The likely physiological effects of airborne metal deposition are difficult to gauge for plants as the majority of toxicity experiments relate toxic effects to root uptake rather than their deposition as particles to leaf surfaces. The concentrations of metals in tree foliage, as a result of root uptake, reported to have a toxicological effect are generally much greater than the concentrations in the present study (Smith and Brennan, 1984; Heale and Omrod, 1982; Carlson and Bazzaz, 1977; Brown and Wilkins, 1985). This suggests that despite the elevated concentrations compared to the control site they are unlikely to result in any direct toxicity to the plant species studied.

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

Despite these elevated concentrations and the observed decline in PM_{10} concentrations within 12 m from each road, distance from the road did not have a consistent affect on metal concentrations in the leaf tissue from the three tree species investigated. Only Cu concentrations in birch and maple leaves were significantly related to the distance from the road. The affect of distance was, however, closely related to the total concentrations of Cd, Cr, Cu, Fe, Ni and Zn in the nettle leaves.

4.2 Differences in metal concentration between plant species

The difference in metal concentrations between species is likely to be due to differences in their leaf arrangement, morphology and/or surface properties. Species with a large number of small, hairy and sticky leaves have been shown to exhibit high particulate capturing efficiencies (Beckett et al., 2000a; Freer-Smith et al., 2004; Freer-Smith et al., 2005). Nettle and birch leaves exhibit these characteristics explaining the greater concentrations observed in the leaves of these species compared with the cypress and maple. Although only Cu concentrations in birch were significantly affected by distance from the road, Cr, Fe and Ni concentrations did appear to be declining. This, together with the fact that metal concentrations in nettle were often greater than those in birch, suggests that if the exposure period had been extended the differences in concentration in birch along the transect may have become more pronounced. The affect of distance on nettle concentrations may have been a function of the smaller height of this species compared with the trees (Smith, 1976). The tree species used in this study were all standards, with heights of between 1.5 to 1.8 m, whereas the nettle plants were positioned on site when their heights were 0.2 m. The nettles are therefore more likely to be exposed to re-suspended road dusts (Fernández Espinosa and Rossini Oliva, 2006) and spray from roads during wet weather than the taller tree species. This is supported by the dramatic decline between the 0 and 2 m distances observed in the nettle tissue concentrations at Park Square Gardens.

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

4.3 Differences in plant leaf concentrations between metals

Leaf concentrations of the eight metals were all positively correlated with each other, suggesting that all metals originate from the same source/s (Monaci et al., 2000). Previous studies have also found that metal concentrations in plant tissues exposed to traffic sources are correlated (Monaci et al., 2000; Riga-Karandinos and Saitanis (2004). Here the correlations between Cd and Fe and Cr, Cu, Fe and Ni were particularly strong and this is likely to represent their particular origins within the overall traffic source. Anthropogenic Fe, Cr and Cu originate primarily from brake wear (Harrison et al., 2003; Monaci et al., 2000; Tasdemir et al., 2005; Wåhlin et al., 2006) and other studies have shown strong correlations between the concentrations of these metals on the surfaces of leaves (Monaci et al., 2000; Riga-Karandinos and Saitanis, 2004). Cd is present in the products of tyre wear and exhaust emissions (Allen et al., 2001; Monaci et al., 2000), the strong relationship between this metal and Cu cannot be explained specifically, as, although they are both present in exhaust emissions, this is also true of several other metals for which the correlations are much weaker (Allen et al., 2001). Harrison et al. (2003), however, found that the size distribution of Cd within particles suggested that it originated primarily from wear rather than combustion which may explain its correlation with Cu. Fe is a crustal metal (Monaci et al., 2000; Tasdemir et al., 2005) and the greater concentrations of this compared to the anthropogenic metals suggests than soil dusts have been re-suspended by tyre shear (Tasdemir et al., 2005). Leaf metal concentrations followed the order Fe>Zn>Ba>Cu>Pb>Cr>Ni>Cd for total concentrations and Zn>Fe>Ba>Cu>Pb, Ni>Cr>Cd for soluble metals. This ordering is similar to that found in other studies investigating the composition of PM_{10} (Allen et al., 2001; Tasdemir et al., 2005), suggesting that the particulate pollution in London is representative of a 'typical' composition.

Total concentrations of Fe were around 5 times greater than those for Zn, whereas soluble concentrations of Zn were around 1.5 times those of Fe. Similarly, total concentrations of Cr were around double those of Ni, whereas soluble concentrations of Ni were around 4 times those of Cr. Their reversal of positions in the ranking of concentrations suggests that significant proportions of the Zn and Ni are in a soluble form (approximately 10% and 13% respectively) compared to a very small proportion of Fe and Cr (approximately 1%). Fe and Cr are primarily present within the coarse ($PM_{2.5-10}$) fraction, whereas Zn and Ni have an even size distribution indicative of a range of sources which may explain why a greater proportion of these metals is in a soluble form (Harrison et al., 2003). Soluble metal fractions were generally lower than fractions measured in the air by other workers. For example, solubility of Cd, Cu, Pb and Zn in atmospheric aerosol has been reported to range from 25-90%, 27-90%, 4-70% and 73-93% respectively (Hoffmann et al. 1997; Fernandez et al. 2002; Voutsa and Samara 2002). It is very difficult to draw conclusions about the relative amount of water-soluble trace metals in particulate matter because it depends on relative contributions of various emission sources to ambient particulate matter and meteorological conditions, both of which vary over time (Tomasevic et al., 2005). Assuming the soluble fraction of metals deposited to trees during the present study were similar to those cited in the literature, then it is evident here that a loss of soluble metal has occurred at some point, most likely through leaf runoff following precipitation which removes water-soluble deposits more rapidly than insoluble deposits (Rodrigo and Avila, 2002). However, the domination of insoluble metals in leaf particulate deposits may also suggest the main components of the particles are derived from road dusts and soil re-suspension (Duan et al., 2005; Manalis et al., 2005). In stable atmospheric conditions, coarse particles, such as these, will deposit very quickly (QUARG, 1996). This is supported by the rapid fall of metal levels away from the road, which is characteristic of coarse particle dispersion (QUARG, 1996).

5 Conclusion

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

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

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

Table 1

Mean soil metal and PM_{10} concentrations (mg/kg and µg/m^3) 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)

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.

Table 2

Correlation co-efficients between the metal concentrations measured in downy birch, Lawson cypress, field maple and common nettle following exposure to particulate pollution from two 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

Table 3

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 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.

	Log metal concentrations (mg/kg)							
Metal	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]

[a]Estimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; [b]Denotes significance, where $P<0.0015$; [c]n=5.

Table 4

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 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 locations.

	Log differences in metal concentrations compared to the rural control site (mg/kg)							
Metal	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*

[a] Estimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; [b] Denotes significance, where P<0.002

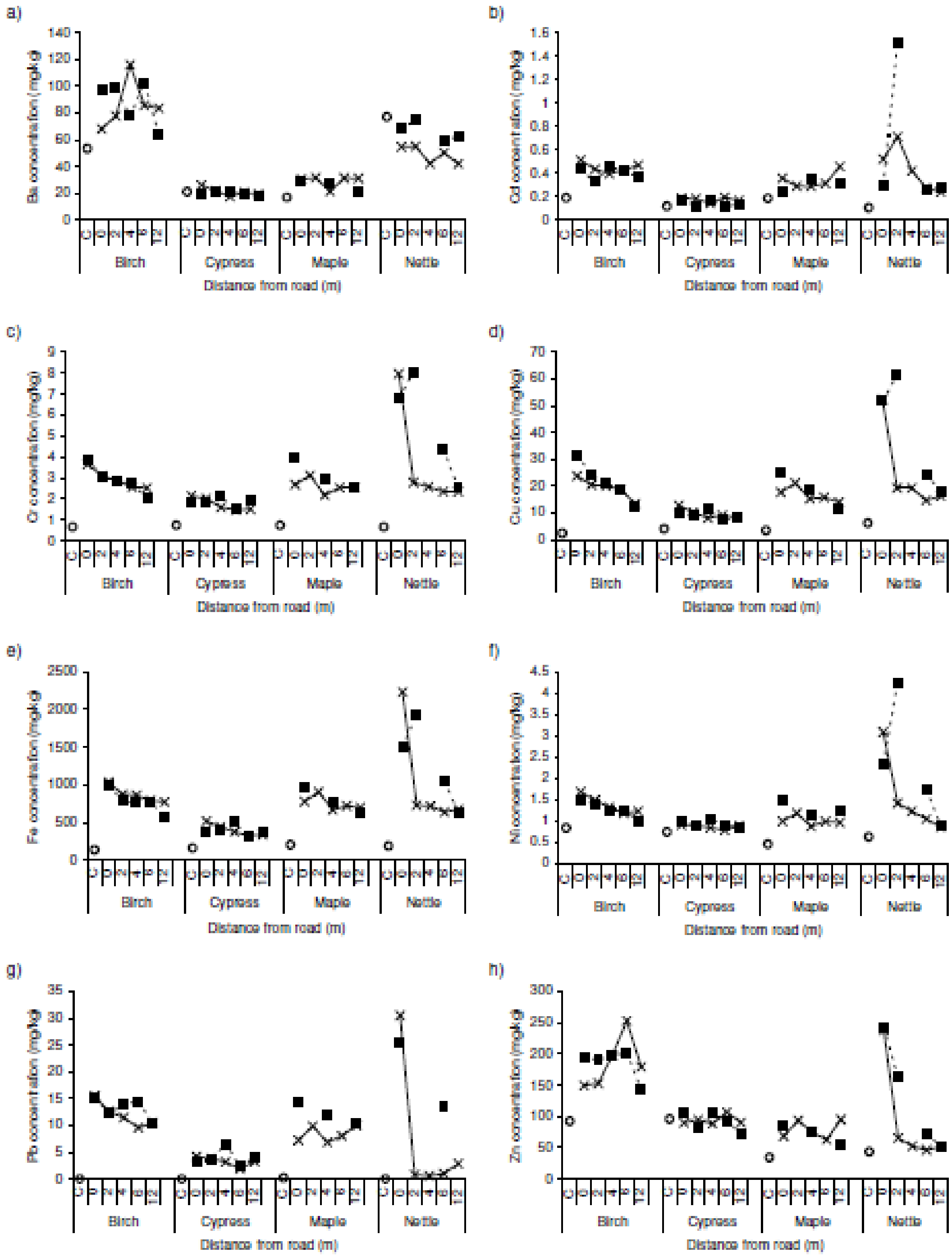
Table 5

Log soluble metal concentrations in leaves of downy birch, Lawson cypress and field maple exposed to particulate emissions at varying distances (up to 12 m) from two heavily polluted London roads at Brompton Square (74 day exposure) and Park Square Gardens (114 day exposure) and the differences 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 locations.

Site		Log soluble metal concentrations at the two London sites and the differences between those from the rural control site (mg/kg)								
	Metal	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
	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
Park Square Gardens	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

[a] Estimated mean from REML analysis, figures in parenthesis are the standard errors of the mean; [b] Denotes significance, where P<0.001

Figure 1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Ba concentration (mg/kg)
140
120
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60
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Birch
Cypress
Maple
Nettle
Distance from road (m)
b)
Cd concentration (mg/kg)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
c)
Cr concentration (mg/kg)
9
8
7
6
5
4
3
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1
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d)
Cu concentration (mg/kg)
70
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30
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e)
Fe concentration (mg/kg)
2500
2000
1500
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500
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f)
Ni concentration (mg/kg)
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4
3.5
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g)
Pb concentration (mg/kg)
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h)
Zn concentration (mg/kg)
300
250
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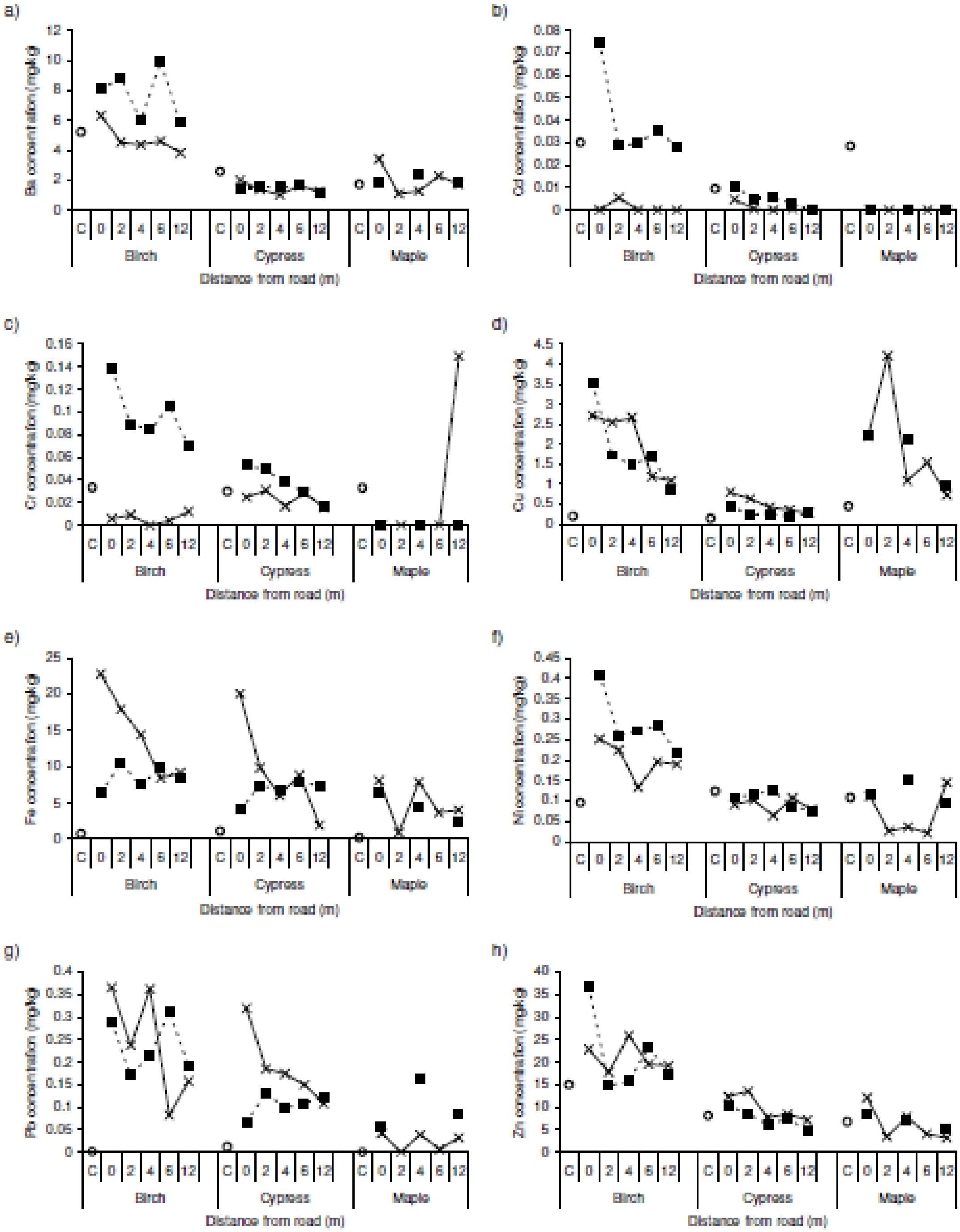
150
100
50
0

Figure 2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b)
Cd concentration (mg/kg)
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c)
Cr concentration (mg/kg)
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d)
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Fe concentration (mg/kg)
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Ni concentration (mg/kg)
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g)
Pb concentration (mg/kg)
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h)
Zn concentration (mg/kg)
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C
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2
4
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12
Birch
Cypress
Maple
Distance from road (m)