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Framework for using deciduous tree leaves as biomonitors for intraurban particulate air pollution in exposure assessment

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Abstract Fine particulate matter ($PM_{2.5}$) air pollution, varying in concentration and composition, has been shown to cause or exacerbate adverse effects on both human and ecological health. The concept of biomonitoring using deciduous tree leaves as a proxy for intraurban PM air pollution in different areas has previously been explored using a variety of study designs (e.g., systematic coverage of an area, source-specific focus), deciduous tree species, sampling strategies (e.g., single day, multi-season), and analytical methods (e.g., chemical, magnetic) across multiple geographies and climates. Biomonitoring is a low-cost sampling method and may potentially fill an important gap in current air monitoring methods by providing low-cost, longer-term urban air pollution measures. As such, better understanding of the range of methods, and their corresponding strengths and limitations, is critical for employing the use of tree leaves as biomonitors for pollution to improve spatially resolved exposure assessments for epidemiological studies and urban planning strategies.

Keywords Biomonitoring · Deciduous tree leaves · Particulate matter · Exposure assessment

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Introduction

Ambient fine particulate matter ($PM_{2.5}$) has been linked to ill health, including cardiovascular and respiratory outcomes (Laden, Neas et al. 2000; Dockery 2001; Pope III, Burnett et al. 2002; Dominici, Peng et al. 2006; Ito, Mathes et al. 2011; Bell 2012), with varying health effects depending on chemical composition (Valavanidis, Fiotakis et al. 2008; Bell, Ebisu et al. 2009; Peng, Bell et al. 2009; Bell, Ebisu et al. 2011; Mostofsky, Schwartz et al. 2012). Although PM concentration and composition varies across urban areas (Eeftens, Tsai et al. 2012; Clougherty, Kheirbek et al. 2013), monitoring costs, particularly given necessary sampling density, may limit extensive monitoring campaigns to relatively short periods of a few weeks or less. Biomonitoring of ambient air pollution using tree leaves typically depends on atmospheric deposition and/or

cellular incorporation, versus uptake from roots and translocation; however, there are various physiological mechanisms, timescales, and environmental factors to consider. Thus, the motivation for this review lies in the potential of biomonitoring using tree leaves as an important component of meeting the growing need for low-cost monitoring methods in the realm of exposure science, in order to capture longer-term, spatially resolved, finer-scale, ambient PM measures across urban space.

With the beginning of the industrial era, effects of increased anthropogenic air pollution on plant and animal organisms were evident (Markert, Oehlmann et al. 1997). In the nineteenth century, qualitative environmental information provided by vegetation was observed in lichens by Scandinavian lichenologist William Nylander (Ågren and Weih 2012). Since then, biomonitoring of air pollution based on quantitative analysis of plants, lichens, and deciduous or evergreen tree leaves has been explored (Maatoug, Taïbi et al. 2012; Moreno, Sagnotti et al. 2003), but not developed for exposure estimations. Specifically, tree leaves may serve as low-cost, widely available biomonitors, especially for non-essential element concentrations (i.e., those not essential for a tree's physiological function and survival) (Kolon, Samecka-Cymerman et al. 2013), due to their quantity, distribution across metropolitan areas, availability of leaves at heights approximating the human breathing zone, and minimal training required for collection (Sawidis, Breuste et al. 2011; Simon, Braun et al. 2011). In recent years, several European studies have demonstrated utility of leaves as biomonitors in urban areas (Baycu, Tolunay et al. 2006), a limited number of US studies have considered tree density or cover as a predictor of spatial variation in pollution (Clougherty, Kheirbek et al. 2013), and no US studies, to our knowledge, have effectively used deciduous tree leaves as biomonitors across an urban area.

In response to the growing need for low-cost methods to assess fine-scale ambient air pollution and composition variation across urban areas, we review the literature on deciduous tree leaves as biomonitors of PM. Specifically, we consider species selection, study design, methods for compositional analysis, and technical and analytical challenges, to assess utility of deciduous tree leaves for intraurban air pollution exposure assessment and source apportionment.

Literature review methods

A search was performed using PubMed and Google Scholar for articles published through the end of 2014, identifiable using the keywords: "deciduous," "trees," "leaves," "biomonitor," "urban," "spatial," "elemental," "air," and either of "particulate" or "PM," returning 550 unique articles. We reviewed titles and abstracts to include studies sampling deciduous tree leaves for analysis of trace element concentrations in urban or area sources of particulate matter pollution ($n = 44$), and studies using either co-located ($n = 6$) or monitoring station ($n = 5$) PM measurements to validate deciduous tree leaf measurements. We excluded studies of coniferous tree or plant species or moss ($n = 118$); non-particulate air pollutants (incl. gases) ($n = 61$); trees as biological filters of air pollution ($n = 10$); or anatomical, morphological, or physiological characteristics of tree leaves for urban habitat quality ($n = 10$). Some studies were excluded based on multiple criteria.

Forty-four studies met all study criteria; methods and results from these studies are reviewed here, structured as to support a design for intraurban air pollution studies seeking to utilize tree leaves for biomonitoring purposes. Articles including multiple tree species, some of which are not deciduous, are included here but the focus is only on the use of deciduous species in that particular study. For a review on use of evergreen trees—specifically conifers—as biomonitors of inorganic air pollutants, see Bertolotti and Gialanella (2014). Studies exploring differences between deciduous and evergreen species (Sawidis 1995; Jordanova et al. 2003; Moreno, Sagnotti et al. 2003; Aboal, Fernández et al. 2004; Baycu, Tolunay et al. 2006; Tomašević, Vukmirović et al. 2008; Yildiz, Kula et al. 2010; Hansard 2011; Sawidis, Breuste et al. 2011; Sant'Ovaia 2012) will not be discussed here.

Results

Species selection

Particle capture efficiency varies with leaf characteristics; complex leaf shape, large surface area, or the

presence of trichomes (hair-like features on leaf surface) can each increase surface adsorption and efficiency of particle collection (Moreno, Sagnotti et al. 2003; Chakre 2006; Sheppard, Hallman et al. 2009). Choosing a tree species with a higher deposition velocity such as trees in the genus *Betula* or *Fagus* (Mitchell 2010) may provide better results with co-located PM samples. Deposition velocity (dry or wet) of PM may be calculated—though complex in nature—taking into account leaf surface area, deposition velocity for different PM size fractions, etc., and varies between tree species, and with wind speed and tree canopy characteristics (i.e., open vs closed). Selecting trees in an open canopy structure is ideal for this calculation, so there is less PM interception from adjacent tree canopies and more interpretable values. Because this calculation requires leaf area, leaf measurements must be made prior to any subsequent analysis that may be irreversibly destructible (e.g., digestion and chemical analysis). The conventional method for calculating deposition velocity involves dividing particle flux to the sampling surface over a known period of time by the ambient concentration (Mitchell 2010). For $PM_{2.5}$ or PM_{10} dry deposition calculations, along with a summary of average deposition velocities by species, refer to Hirabayashi, Kroll et al., (2012). Further, PM resuspension from leaves may be estimated using wind speed and unit leaf area information though the need for this may be less important when utilizing tree leaves with trichomes, or "hairy" surfaces may prevent particle loss or resuspension compared to smooth leaf surfaces. Though wet deposition velocity may be calculated, planning leaf sampling campaigns around wet weather events may exclude this from consideration.

The majority of studies reviewed here selected species by abundance within, or spatial coverage across the sampling domain (Matzka 1999; Tomašević, Vukmirović et al. 2008; Tomašević and Aničić 2010; Tomašević, Aničić et al. 2011; Petrova, Yurukova et al. 2012; Petrova, Yurukova et al. 2014; Rai and Chutia 2014; Rodriguez-Germade, Mohamed et al. 2014; Šerbula, Radojevic et al. 2014), while others considered leaf surface characteristics (e.g., broad shape, ridged, or "hairy" surface) to maximize surface deposition (Kardel 2011; Kardel, Wuyts et al. 2012; Petrova, Yurukova et al. 2012; Sant'Ovaia 2012), or temperature and soil tolerance (i.e., ability to grow in almost any type of soil) (Šerbula, Miljkovic et al. 2012). Using nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) digestion and

inductively coupled plasma atomic emission spectrometry (ICP-AES), Piczak (2003) observed the highest concentrations of Al, Ca, Cr, Cu, Fe, Mg, Ni, Pb, Sr, and Ti in *Tilia platyphyllos* leaves versus *Salix fragilis*, *Acer platanoides*, and *Betula verrucosa*, but concluded that *A. platanoides* and *B. verrucosa* were good biomonitors for Mn and Fe due to relatively higher particle accumulation potential (i.e., relatively larger surface area and doubly serrated leaf margins which allow for increased particle deposition). It is worth noting that authors found species-, location-, and time-dependent differences in heavy metal concentrations—specifically Al, Ba, Fe, Mn, and Zn—(excluding Ti) in all sampled species; however, authors did determine that all sampled tree species were sufficient biomonitors for Cd and Pb pollution (Piczak 2003). Through morphological and anatomical analysis of *Carpinus betulus* and hairy *Tilia* sp. leaves, Kardel (2011) and Kardel, Wuyts et al. (2012, 2013) determined that hairs, veins, or a rugose surface decreased boundary layer resistance of leaves, leading to more efficient particle accumulation than smooth, waxy leaves.

Interspecies comparisons among trees were explored by many authors finding—in some cases—substantially different results in magnetic particle, heavy metal, or isotope collection efficiency (Hanesch 2003; Jordanova et al. 2003; Piczak 2003; Baycu, Tolunay et al. 2006; Tomašević, Vukmirović et al. 2008; Power, Worsley et al. 2009; Mitchell 2010; Šućur 2010; Kardel 2011; Kardel, Wuyts et al. 2012; Kardel, Wuyts et al. 2013). Mitchell (2010) measured leaf saturation isothermal remanent magnetization (SIRM) to compare the magnetic particle-capturing ability of *T. platyphyllos*, *Betula pendula*, *Salix alba*, *Quercus robur*, *Acer campestre*, *Fagus sylvatica*, *Fraxinus excelsior*, *Acer pseudoplatanus*, *Sambucus nigra*, and *Ulmus procera* leaves. The authors inferred relatively greater magnetic particle deposition velocities for *T. platyphyllos* and *F. sylvatica*—2.4 and 3.0 cm s^{-1}, respectively—from the presence of more magnetic particles per unit leaf area, as well as secretion of a waste product by aphids resulting in sticky leaf surfaces (for *T. platyphyllos*). Using HNO_3 and H_2O_2 digestion and ICP-MS analysis, Petrova, Yurukova et al. (2014) found that *B. pendula* was a better bioaccumulator for Cd, Cr, and Zn, compared to *A. platanoides* and *Aesculus hippocastanum*, while *A. platanoides* better accumulated Fe. These constituents (Cd, Cr, and Fe) along with Pb were found to be influenced more by sampling location, and less by

variation in uptake by tree species, though Zn concentrations were found to be more influenced by tree species (Petrova, Yurukova et al. 2014). Lastly, using HNO$_3$ and H$_2$O$_2$ microwave digestion and inductively coupled plasma optical emission spectrometry (ICP-OES), Alagić, Šerbula et al. (2013) determined that roots and leaves of *Betula* species yields more useful data on environmental As and Cd than *Tilia* species. Deljanin, Tomašević et al., (2014) concluded that a greater variation in Pb isotopic compositions among trees indicated higher species sensitivity and therefore improved Pb source identification. *B. pendula* leaves, because of their relatively thicker epicuticular wax layer, had the highest PM accumulation and widest range of ^{206}Pb/^{207}Pb ratios for both washed (1.146–1.192) and unwashed leaves (1.146–1.185).

A challenge in the literature has been determining ideal deciduous tree species for PM collection in highly polluted areas over time, providing quality spatiotemporal data for areas where human exposure assessment may be needed. Thus, ability to grow in urban environments is important for sampling in highly polluted areas, as well as consistency in species availability and survival across an urban domain. When considering duration of PM collection on leaves, Power, Worsley et al. (2009) concluded that *Tilia europaea* versus *A. pseudoplatanus* leaves may be representative of PM accumulation over time due to their more efficient particle removal capability. Because *A. hippocastanum* reflected atmospheric concentrations of trace metals, both Tomašević, Vukmirović et al. (2005, 2008) and Aničić, Spasić et al. (2011) concluded it to be suitable for urban PM collection. Likewise, Tomašević and Aničić (2010) concluded that *A. hippocastanum* is an appropriate biomonitor for atmospheric Pb and Cu in highly polluted areas.

Easily identifiable, generalist species should be considered for use in biomonitoring studies. Easily identifiable tree species may facilitate collection and improve consistency across sampling personnel. Trees capable of thriving in multiple environments ("generalists") may improve comparability across studies and locations, as would the capacity to grow at different elevations and the ability to transplant well (Muxworthy, Matzka et al. 2003). However, diversity of tree geno- and phenotypes across these different environments may complicate straightforward species comparisons. Relatedly, geographic range of selected deciduous tree species can be a limiting factor for sampling allocation; hence, most studies prioritize spatial coverage across study areas during species selection.

Sheppard, Hallman et al. (2009) determined that tree species was not a strong determinant of spatial variability of W and Co, despite the lack of species consistency across their sampling domain, and attributed non-specificity to the similarity of leaf characteristics among sampled species—*Ulmus*, *Morus*, *Populus*, and *Fraxinus*. Some of these studies have demonstrated that individual tree species provide data on PM pollution, but those examining multiple tree species may provide comparative insight into a representative deciduous tree species for PM biomonitoring.

Guidance on species selection for biomonitoring efforts is dependent on study hypotheses. For example, systematically sampling leaves of similar age, orientation, and height on the same deciduous species across time and space may provide information on seasonal or annual human exposures to ambient PM if samples were taken near the human breathing zone. Alternatively, perimeter sampling of trees around a fixed source or along major roadways may provide a cost-effective means of obtaining data on pollutant emissions and dispersion. For direction on longer-term biomonitoring efforts, evergreen tree species may be more appropriate; refer to Bertolotti and Gialanella (2014).

Site selection

Site allocation approaches are hypothesis-dependent and have ranged from systematic coverage (i.e., representation across land-use types) (Kardel 2011; Kardel, Wuyts et al. 2012; Petrova, Yurukova et al. 2012; Šerbula, Miljkovic et al. 2012; Kardel, Wuyts et al. 2013; Petrova, Yurukova et al. 2014) to source-specific sampling (i.e., high-traffic or industrial areas) (Moreno, Sagnotti et al. 2003; Baycu, Tolunay et al. 2006; Samecka-Cymerman, Kolon et al. 2008; Power, Worsley et al. 2009; Sheppard, Hallman et al. 2009; Mitchell 2010; Tomašević and Aničić 2010; Tomašević, Aničić et al. 2011; Alagić, Šerbula et al. 2013; Kolon, Samecka-Cymerman et al. 2013; Šerbula, Kalinovic et al. 2013; Šerbula, Radojevic et al. 2014). Studies have collected leaf samples from areas of varying land use, in an attempt to first identify then distinguish between air pollution sources by land-use type (e.g., urban city center, park, or green space). To compare leaf samples by land-use type, Kardel et al. (2011) and Kardel, Wuyts et al. (2012, 2013) sampled sites across green spaces,

suburban areas, urban areas, and harbor/industrial areas. Šerbula, Miljkovic et al. (2012) sampled within a domain divided into five zones: (1) urban-industrial, (2) suburban, (3) rural, (4) tourist, and (5) control; however, details regarding the methodological division of the sampling domain into these zones were not included.

To systematically sample leaves across different urbanization levels, Davila, Rey et al. (2006) divided their urban and suburban zones into 1 km^2 cells, and the city center (expecting greater spatial variability) into 0.25 km^2 cells. Power, Worsley et al. (2009) focused sampling along heavily trafficked roadways, to compare roadside pollution along four differently characterized roadways. Based on an urban gradient scheme, Petrova, Yurukova et al. (2014) selected sampling sites ($n = 5$), which divided the city (Plovdiv, Bulgaria) into urban, suburban, and industrial sectors allowing for source variation (e.g., industrial power plants, high-traffic areas). Likewise, Petrova, Yurukova et al. (2012) divided their sampling domain into the following five "different areas of anthropogenic pressure" using a global positioning system (GPS): (1) nature monument, (2) park, (3) neighborhood, (4) vegetable crops, and (5) railway station.

Alternatively, Aboal, Fernández et al. (2004) selected sampling sites in rural areas at least 300 m from main roads and populated areas using the following criteria to compare deciduous species to evergreen and mosses: (1) inclusion in protected areas, (2) homogenous distribution within a regular grid of 20 × 20 km, and (3) in situ election of patches of representative vegetation, of minimum area of 0.5 hectares (ha). One aim of this study was to determine the extent to which atmospheric deposition contributes to metal concentrations in leaves and needles, though no measurement of atmospheric deposition was considered in this study. This approach seems more appropriate for determination of "background" concentrations in the tissues of different types of plant species (i.e., deciduous, evergreen, and moss) versus validation with PM measurements, as sample preparation did not allow for proper determination of PM size due to the cleaning, washing, and homogenization of samples in a laboratory blender prior to elemental analysis. Other studies used systematic grid-based approaches to achieve uniform coverage, irrespective of land-use type or source density. Hanesch (2003) used an urban administration grid to allocate at least one sampling point to each cell.

A sampling strategy may be more efficient and provide source-specific information by considering such variables as traffic density, elevation gradients, etc., in a systematic sampling scheme, as general "urban" and "suburban" classifications may encompass multiple source contributions in varying concentrations, which—depending on analytical methods—presents difficulty in teasing apart vehicular versus bus or railway traffic, for example.

Sampling height and leaf position

Sampling height may depend on study hypotheses, characteristics of emission sources relative to leaf position, or characteristics of selected trees. Because PM concentration and composition can vary with height or source proximity, it is important to keep this variable constant to accurately compare between sites. Studies reviewed here sampled at heights ranging from less than 1 to more than 5 m above ground, depending on tree height and crown properties (Kardel, Wuyts et al. 2012; Petrova, Yurukova et al. 2012;Sadeghian 2012; Kardel, Wuyts et al. 2013; Kolon, Samecka-Cymerman et al. 2013; Šerbula, Radojevic et al. 2014), desired leaf age or availability (Matzka 1999; Maher 2008; Mitchell 2009; Power, Worsley et al. 2009; Sant'Ovaia 2012), position of leaves (e.g., facing roadside, in all cardinal directions) (Davila, Rey et al. 2006; Kardel 2011; Sant'Ovaia 2012; Kardel, Wuyts et al. 2013; Šerbula, Kalinovic et al. 2013; Hofman, Wuyts et al. 2014; Petrova, Yurukova et al. 2014), or hypothesized associations between concentrations and near-roadway pollution gradients (Hofman, Stokkaer et al. 2013). One study did not specify sampling height (Baycu, Tolunay et al. 2006). Hofman, Stokkaer et al. (2013) found leaf SIRM 66 % weaker, on average, for leaves collected at 12 versus 5 m in height within an urban street canyon in the first study to examine the relationship between sampling height and leaf SIRM at small spatial scales within single tree crowns (Hofman, Stokkaer et al. 2013). In addition, authors found significant effects in leaf SIRM variation by height ($p < 0.0001$) and azimuthal position ($p < 0.0001$), but not by tree position; plotting all leaf SIRM values against respective sampling heights showed an exponential decrease in SIRM ($R^2 = 0.50$) within all individual sampled tree crowns (Hofman, Stokkaer et al. 2013). Authors concluded that air circulation and sampling height were the main parameters influencing leaf SIRM measurements; their findings

provide valuable insight into the spatial distribution of PM within a street canyon (Hofman, Stokkaer et al. 2013). Mitchell (2009) found 50 % reduction in SIRM from leaves collected at 2 versus 0.3 m in height. Findings regarding leaf height effects on measured PM and constituents are mixed. Maher (2008) observed significant height effects, wherein SIRM, Pb, and Fe concentrations all peaked at 0.3 m, and decreased with height, while Zn, Ba, and Mn were lowest at 0.3 m, and increased with height. Another study found no significant effect of leaves sampled between 1.5 and 5 m on leaf SIRM (Kardel, Wuyts et al. 2012).

Beyond sampling height, appropriate study designs for leaf sampling require attention to the position of selected leaves on the tree, as leaves adjacent to a busy road, for example, may differ in PM deposition from leaves on the opposite side. Further variation may arise from position on a branch, leaf size, age, light, and shade conditions, though this variation may be assessed by sampling multiple leaves per branch, and selecting leaves of uniform size (Guha and Mitchell 1965) or of similar age (i.e., oldest leaves on newest twig growth) (Matzka 1999; Maher 2008; Sadeghian 2012). Leaves exposed to relatively more sunlight may accumulate more heavy metals then those in the shade due to increased transpiration rates, therefore resulting in different metal concentrations within the same crown (Luyssaert, Raitio et al. 2002). This aspect of study design becomes particularly important for studies that focus on isotope compositions, as specific conditions (e.g., relative location within the canopy) at each sampling site may influence isotopic ratios (Deljanin, Tomašević et al. 2014). Therefore, leaf-based sampling design should reflect study hypothesis and account for the variation in constituents of atmospherically deposited PM measured from different positions and height on trees.

Season and sampling interval

Deciduous tree leaves are generally appropriate for pollution measurement during the growing season (i.e., May through September or October) or a portion of it (e.g., spring season of May through June). For year-round or longer-term measures, non-deciduous evergreens or semi-evergreens may be more appropriate, as their leaves or needles slowly incorporate particles into the thick epicuticular wax layer over longer growing periods (Mitchell 2010).

For ambient air pollution monitoring, seasonal characteristics (e.g., meteorology, regional source emissions intensity) are important drivers of temporal variance in PM concentrations (Bereznicki, Sobus et al. 2012). For leaf sampling, the seasonal growth cycle is of concern. Single-season sampling ((i.e., spring (Mitchell 2010) or summer (Maher 2008; Yildiz, Kula et al. 2010; Simon, Braun et al. 2011; Tomašević, Aničić et al. 2011; Sadeghian 2012; Alagić, Šerbula et al. 2013; Hofman, Stokkaer et al. 2013; Kolon, Samecka-Cymerman et al. 2013; Petrova, Yurukova et al. 2014)) may be useful for capturing specific meteorological or regional source emissions regimes. Autumn sampling (Matzka 1999; Davila, Rey et al. 2006; Mitchell 2009; Sheppard, Hallman et al. 2009; Dogan, Unver et al. 2014; Šerbula, Radojevic et al. 2014)—assuming leaf persistence—is useful for capturing PM accumulated throughout the growing season. However, interpreting results from longer-term sampling campaigns may be complex due to variables discussed throughout this paper (e.g., PM resuspension, meteorological events). Alternatively, multi-season approaches have been used to compare pollutant concentration and composition across seasons, and biomonitoring capability of trees at different points in the growing season (Sawidis 1995; Aboal, Fernández et al. 2004; Šućur 2010; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Hansard 2011; Kardel 2011; Kardel, Wuyts et al. 2012; Sant'Ovaia 2012; Hofman, Wuyts et al. 2014; Rodriguez-Germade, Mohamed et al. 2014). A variable that is introduced in multi-season sampling campaigns is growth dilution of leaf biomass, which may present uncertainty in interpretation of PM or heavy metal concentrations. For deciduous trees, this occurs largely as the spring seasons turns to summer, but tree leaves do not emerge in synchrony (Lechowicz 1984).

While longer sampling intervals may be useful to compare accumulated seasonal concentration gradients across an urban area, shorter intervals may be useful for examining short-term weather or source effects on PM deposition on leaves. Matzka (1999) used consecutive-day sampling to examine spatial and temporal patterns of urban dust on roadside tree leaves ($n = 600$). Others used consecutive-day sampling to elucidate patterns of PM magnetism from varying vehicular emissions (Maher 2008; Mitchell 2009). Hofman, Wuyts et al.'s (2014) entire in-leaf season sampling campaign (i.e., from May to November) revealed a 263 % higher leaf SIRM for unwashed leaves collected in September

versus May, and 380 % leaf SIRM increase in washed samples of the same sampling period. This is similar to Kardel's (2011) result of 288 and 393 % increases in washed versus unwashed leaf SIRM values, respectively. Following HNO_3 and H_2O_2 digestion and ICP-MS analysis, Tomašević and Aničić (2010) observed a statistically significant increase in Cr, Fe, Ni, Zn, and Pb measured in *A. hippocastanum* leaves from 2002 to 2006 (May and September) in Belgrade, Serbia, indicating an accumulation throughout the growing season. However, it was hypothesized that Cu translocated from senescent to non-senescent tree parts, making it difficult to parse out Cu as an essential constituent of plant tissues versus accumulation via atmospheric deposition (Tomašević and Aničić 2010). Therefore, PM analyzed from tree leaves may provide spatiotemporal information about seasonal or entire in-leaf growing season concentrations, depending on study design. However, various physiochemical properties affecting the interpretation of various PM constituents must be best accounted for depending on sampling period, soil, and leaf characteristics.

Physiochemical properties affecting interpretation of PM contribution to leaves

When utilizing leaves as biomonitors for air pollution, it is important to determine what proportion of PM on—or in—leaves results from airborne deposition versus translocation of elements used as markers for PM from roots, bark, or soil. Pollutant accumulation varies within different parts of plants or trees (Dogan, Unver et al. 2014). For larger-scale studies that may include multiple or national or subnational area(s), consideration of pedogenic processes is necessary to disentangle magnetism of anthropogenic pollution from a variably magnetic soil background (Liu, Roberts et al. 2012). Generally, magnetic materials of industrial origin have larger magnetic grain sizes compared to biogenic or natural magnetic materials, indicated by various magnetic measurements (e.g., ARM/SIRM) (Liu, Roberts et al. 2012). More specifically, there is a positive relationship between magnetic materials from fossil fuel combustion and heavy metals in PM (Liu, Roberts et al. 2012). For magnetite (which has natural and anthropogenic origins) there are identification criteria for biogenic magnetite determination (e.g., Moskowitz test), but these do not always guarantee accurate results (Liu, Roberts et al. 2012). However, Rodríguez-Germade, Mohamed et al.

(2014) suggested that biogenic magnetic materials in leaves are not significantly related to those in soil, indicating a predominant contribution from airborne deposition (Rodriguez-Germade, Mohamed et al. 2014). Using translocation and mobility parameters, Šerbula, Miljkovic et al. (2012) found that though present in soil, Cd, Hg, and As were not detected in the leaves, branches, or roots of *Robinia pseudoacacia*. However, Alagić, Šerbula et al. (2013) suggested that this translocation factor (TF) (which indicates the ratio of trace metals in above-ground plant parts to those in the plant root) may not be a reliable estimator of metal translocation from root to leaves for As and Cd, due to the fact that high TF values may be a consequence of contribution from direct absorption of As and Cd through leaves to total foliar concentrations.

While some elements are relatively hard to mobilize from soil (e.g., Pb), translocation of inorganic elements within plants is complex (Guha and Mitchell 1966). Physiochemical soil characteristics may affect element uptake and bioavailability of elements, and thus should be sampled in conjunction with leaves. Likewise, lower pH may increase bioavailability of metals for uptake (Tomašević, Vukmirović et al. 2008) and pH between 7.1 and 7.7 in clay rich soil limits mobility of heavy metals and iron oxides (Jordanova et al. 2003). If feasible, measuring or obtaining soil pH from sampling sites may be helpful when considering the aforementioned effects of soil pH on uptake and bioavailability. Further, uptake via leaf stoma may potentially reduce interpretability of such PM constituents as Ca, K, and Mg, which are present in a range of macronutrient concentrations because of their essential value to the growth and maintenance of leaf tissue (Raven 2002). However, the extent of uptake via leaf stoma is not clear (Hofman, Wuyts et al. 2014). In addition, a study on seasonal differences in several deciduous tree genera or species (e.g., *Platanus*, *Fagus*, and *Aesculus hippocastanum*) determined some seasonal differences in concentrations of inorganic elements: higher Co, Ni, Mo, Fe, Pb, V, Ti, Cr, and Cu in immature spring samples collected in June and lower concentrations of Co, Ni, Mo, Fe, Pb, V, Ti, Mn, and Ca in autumn samples (Guha and Mitchell 1965). These decreased concentrations reflect back-translocation from the leaves prior to leaf fall (to the ground), though this period of translocation may be too short-lived to capture in a sampling session since senescence occurs not long after (Guha and Mitchell 1966), which is accompanied by closure of leaf stoma and

cessation of epicuticular wax production and subsequent reduction of PM encapsulated into the leaf tissue (Hofman, Wuyts et al. 2014).

In an effort to tease apart natural versus anthropogenic contributions, various authors have calculated enrichment factors (EFs) for leaf samples and in some cases, for bulk PM data collected at sites, which may improve interpretation of results (Samecka-Cymerman, Kolon et al. 2008; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Šerbula, Miljkovic et al. 2012; Alagić, Šerbula et al. 2013; Šerbula, Kalinovic et al. 2013; Rodriguez-Germade, Mohamed et al. 2014; Šerbula, Radojevic et al. 2014). The formula EF = $(E/R)_{sample}$/$(E/R)_{crust}$ represents the ratio of element E and reference element R in the sample $(E/R)_{sample}$ and in the Earth's crust $(E/R)_{crust}$ (Tomašević and Aničić 2010; Aničić, Spasić et al. 2011). Another version of this formula is EF = $C_{plant}/C_{background}$, used by Šerbula, Miljkovic et al. (2012), Šerbula, Kalinovic et al. (2013), and Alagić, Šerbula et al. (2013), where C_{plant} and $C_{background}$ are metal concentrations in leaves from polluted sampling sites and the background site, respectively.

Bioconcentration and translocation factors were calculated by Šerbula, Miljkovic et al. (2012) and Šerbula, Kalinovic et al. (2013) to determine elemental uptake by different tree parts, including roots, branches, and leaves. Findings from both studies indicate a different contribution from topsoil, though both were conducted in Bor, Serbia with average soil pHs greater than seven; soil contribution via absorption was not considered (Šerbula, Miljkovic et al. 2012) and sampled topsoil composition contributed to heavy metal contamination of leaves (Šerbula, Kalinovic et al. 2013). Trees may behave differently (i.e., uptake of pollutants) between sampling sites with varying air pollution concentrations, but spatial variability in soil chemical properties between sites, in addition to different organic compounds released by the roots of each species, may also contribute to measured concentrations in leaf tissue (Šerbula, Kalinovic et al. 2013). Using Fe as the reference element, Aničić, Spasić et al. (2011) and Tomašević and Aničić (2010) determined that EFs for leaf samples and PM were highest for Pb, followed by Zn and Cu, indicating anthropogenic origin, while Ni and Cr were the least enriched. Additionally, EFs for measured bulk PM deposition in Tomašević and Aničić (2010) followed the same pattern for Pb, Zn, and Cu in *A. hippocastanum* and *Tilia* spp., but no agreement

was observed between the accumulation trend of Cr, Fe, Ni, and Zn in leaves versus bulk PM deposition rates. In contrast, application of an EF by Rodríguez-Germade, Mohamed et al. (2014) did not improve correlations among data. A slightly different approach by Maher (2008) explored a mean enrichment ratio of roadside:background for leaf SIRM, Pb, Fe, Zn, Mn, and Ba, finding higher roadside enrichment for SIRM, Fe, and Pb and limited enrichment for Zn, Mn, and Ba. Using Al as the normalizing element in their EF calculations to reflect the amount of silicate in aerosols, Samecka-Cymerman, Kolon et al. (2008) calculated mean EFs for samples ($n = 25$) which revealed enrichment for Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in *Larix decidua* needles, associated with emissions from nearby coke and sulfuric acid-producing factories, as well as nearby municipal thermal-electric power stations; authors used this finding to conclude *L. decidua* to be a potentially powerful biomonitor for Co, Cu, Ni, and Pb pollution. Šerbula, Radojevic et al. (2014) calculated EFs indicating environmental pollution (i.e., EF > 2), for Zn and Mn in birch leaves near a copper smelter; Cu in birch branches had EF > 2.

Another parameter examined by Šerbula, Kalinovic et al. (2013) is the translocation index ($R_{l/b}$), which is a parameter to assess elemental availability in soil and accumulation by or atmospheric deposition on various tree parts; inputs for $R_{l/b}$ include soil, root, branch, and leaf concentrations. Authors found that EFs for linden leaves did not indicate environmental pollution for any investigated constituent (EFs < 2 for Pb, Cu, Mn, and Zn). Despite some studies' usage of crustal composition in EF formulas to determining background concentrations, it has been demonstrated that normalizing element concentrations using average total crust values are inadequate for the following reasons: variable composition of the Earth's crust at any given point compared to a global average; the natural fractionation of elements during their transfer from the crust to atmosphere through weathering and other processes; and the differential solubility of minerals in weaker chemical digestions used in environmental studies (Reimann and Caritat 2000). A more accurate EF might be calculated using concentrations from leaves in polluted versus background sampling sites, for example, while controlling for such factors as soil heterogeneity. Ultimately, the uptake of heavy metals by tree roots is affected by the availability of metals, determined by total heavy metal concentration in soil as well as soil pH (Luyssaert, Raitio et al.

Table 1 Analytic techniques in deciduous tree leaf biomonitoring studies modified after Rai (2013)

Chemical

Parameters	Instrumentation	Studies used	Units	Description
Measured[a]				
Trace element or isotopic determination	Mass spectrometer [inductively-coupled plasma mass spectrometry (ICP-MS)] (Sheppard, Hallman et al. 2009, Šućur 2010, Tomašević and Aničić 2010, Tomašević, Aničić et al. 2011, Petrova, Yurukova et al. 2012, Tomašević, Antanasijević et al. 2013, Deljanin, Tomašević et al. 2014, Petrova, Yurukova et al. 2014), optical emission spectrometry (ICP-AES)] (Piczak 2003, Davila, Rey et al. 2006, Aničić, Spasić et al. 2011, Simon, Braun et al. 2011, Šerbula, Miljkovic et al. 2012, Alagić, Šerbula et al. 2013, Šerbula et al. 2013, Kalinovic et al. 2013, Rodriguez-Germade, Mohamed et al. 2014, Šerbula, Radojevic et al. 2014) Simultaneous sequential inductively-coupled plasma emission spectrophotometry (SIMSEQ) (Samecka-Cymerman, Kolon et al. 2008) Atomic absorption (AA) spectroscopy (Sawidis 1995, Aboal, Fernández et al. 2004, Baycu, Tolunay et al. 2006, Samecka-Cymerman, Kolon et al. 2008, Yildiz, Kula et al. 2010, Sawidis, Breuste et al. 2011, Sant'Ovaia 2012, Šerbula, Miljkovic et al. 2012, Kolon, Samecka-Cymerman et al. 2013, Dogan, Unver et al. 2014) Differential pulse anodic stripping voltammetry (DPASV) with hanging mercury drop electrode (Tomašević, Vukmirović et al. 2005, Tomašević, Vukmirović et al. 2008)	Šućur (2010) Simon, Braun et al. (2011) Piczak (2003) Aničić, Spasić et al. (2011) Rodriguez-Germade, Mohamed et al. (2014) Davila, Rey et al. (2006)Sheppard, Hallman et al. (2009) Tomašević, Aničić et al. (2011) Tomašević, Antanasijević et al. (2013) Šerbula, Kalinovic et al. (2013) Šerbula, Radojevic et al. (2014) Petrova, Yurukova et al. (2012, 2014) Šerbula, Miljkovic et al. (2012) Tomašević and Aničić (2010) Alagić, Šerbula et al. (2013) Deljanin, Tomašević et al. (2014) Samecka-Cymerman, Kolon et al. (2008) Sawidis, Breuste et al. (2011) Sawidis (1995) Aboal, Fernández et al. (2004) Sant'Ovaia (2012) Baycu, Tolunay et al. (2006) Yildiz, Kula et al. (2010) Kolon, Samecka-Cymerman et al. (2013) Dogan, Unver et al. (2014) Šerbula, Miljkovic et al. (2012) Samecka-Cymerman, Kolon et al. (2008) Tomašević, Vukmirović et al. (2005, 2008)	$\mu g\ g^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $ppb\ m^{-2}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ $mg\ kg^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$ n/a $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $mg\ kg^{-1}$ $\mu g\ g^{-1}$ $\mu g\ g^{-1}$	Analysis for elements or isotopes comprising leaf sample

Magnetic

Parameters	Instrumentation	Studies used	Units	Description
Measured[a]				
Magnetic susceptibility (mass χ or volume κ)	Bartington MS2B dual-frequency susceptibility sensor connected to MS2 susceptibility meter (Power, Worsley et al. 2009, Mitchell 2010), Bartington susceptibility meter (Mitchell 2009, Mitchell 2010), Geofyzika KLY 2 Kappabridge (Hanesch 2003), AGICO Kappabridge KLY-4S model (Sant'Ovaia 2012), AGICO Kappabridge KLY-2 instrument (Jordanova et al. 2003, Moreno, Sagnotti et al. 2003)	Power, Worsley et al. (2009) Mitchell (2009) Mitchell (2010) Hanesch (2003) Sant'Ovaia (2012) Moreno, Sagnotti et al. (2003) Jordanova et al. (2003)	$m^3\ kg^{-1}$ A A m $m^3\ kg^{-1}$ $m^3\ kg^{-1}$ $m^3\ kg^{-1}$	Defined as the ratio of magnetization induced to intensity of magnetic field that is measured on volume (κ) or mass (χ) specific basis (Moskowitz 1991, Rai 2013) Studies have explored range of susceptibility measurements: 1) room temperature, 2) frequency-dependent, and 3) low and high temperature, as properties of different classes of magnetic materials behave differently under different conditions.
Frequency-dependent susceptibility (χ_{FD})	MS2 Bartington magnetic susceptibility sensor (Jordanova et al. 2003, Rodriguez-Germade, Mohamed et al. 2014)	Rodriguez-Germade, Mohamed et al. (2014) Jordanova et al. (2003)	$m^3\ kg^{-1}$ %	Measured in terms of frequency variations (calculated as: $\chi_{FD} = \chi_{LF} - \chi_{HF}$) that is used to constrain grain size and domain

Table 1 (continued)

Chemical	Instrument / Studies used	Studies used	Units	Description
				state of magnetic materials (Dearing 1994); inform relative contribution of submicrometre superparamagnetic magnetite grains in a sample (Jordanova, Jordanova et al. 2003)
Anhysteretic remanent magnetization (ARM)	Molspin (Newcastleupon-Tyne, England) A. F. Demagnetizer (Power, Worsley et al. 2009)	Power, Worsley et al. (2009)	$Am^2\,kg^{-1}$	Magnetization acquired by effects of large alternating (AC) current and small direct current (DC) field (Moskowitz 1991)
Isothermal remanent magnetization (IRM)	Cryogenic magnetometer (CCL Ltd.) (Matzka 1999, Maher 2008, Sadeghian 2012); Digico spinner magnetometer (Molyneux-Newcastle) (Hanesch 2003); High sensitivity Molspin Minispin magnetometer (Sant'Ovaia 2012); Molspin Minispin spinner magnetometer (Rodriguez-Germade, Mohamed et al. 2014)	Maher (2008), Matzka (1999), Sadeghian (2012), Hanesch (2003), Sant'Ovaia (2012), Rodriguez-Germade, Mohamed et al. (2014)	A, A, A, A, $Am^2\,kg^{-1}$, n/a	Magnetization left after steady field (1-1000mT) applied for short time (~100 s) then removed (Moskowitz 1991)
Saturation isothermal remanent magnetization (SIRM)	Molspin Minispin magnetometer (Mitchell 2009, Mitchell 2010, Kardel 2011, Hansard, Maher et al. 2012, Kardel, Wuyts et al. 2012, Sant'Ovaia 2012, Hofman, Stokkaer et al. 2013, Kardel, Wuyts et al. 2013, Maher, Ahmed et al. 2013, Hofman, Wuyts et al. 2014); AGICO magnetometer (Davila, Rey et al. 2006, Mitchell 2009); Molspin1A magnetometer (Power, Worsley et al. 2009); 2G Enterprises 755R cryogenic Magnetometer (Moreno, Sagnotti et al. 2003)	Kardel (2011), Kardel, Wuyts et al. (2012, 2013), Mitchell (2010), Hansard, Maher et al. (2012), Hofman, Stokkaer et al. (2013), Hofman, Wuyts et al. (2014), Sant'Ovaia (2012), Mitchell (2009), Davila, Rey et al. (2006), Mitchell (2009), Power, Worsley et al. (2009), Moreno, Sagnotti et al. (2003)	A, A, A, Am^2, A, $Am^2\,kg^{-1}$, A, $Am^2\,kg^{-1}$, A, $Am^2\,kg^{-1}$, $m^3\,kg^{-1}$	Magnetization when external field is reduced to zero and reflective of all concentrations of all remanence-carrying minerals in the sample, dependent on grain size, domain, and temperature (Gubbins and Herrero-Bervera 2007)
Coercivity (H_c)	Variable Field Translation (Jordanova et al. 2003)	Jordanova et al. (2003)	mT	Intensity of applied magnetic field required to reduce magnetization to zero after the magnetization of the sample has been driven to saturation
Calculated[b]				
Parameters		Studies used	Units	Description
High field isothermal remanent magnetization (HIRM)		Hansard (2011), Hansard, Maher et al. (2012), Mitchell (2009), Sant'Ovaia (2012)	%, %, %, $Am^2\,kg^{-1}$	Magnetization acquired between 300mT and 1 T which indicates high-coercivity antiferromagnetic minerals (Hansard 2011)
SIRM/χ		Sant'Ovaia (2012), Moreno, Sagnotti et al. (2003), Sant'Ovaia (2012)	k Am^{-1} Sant'Ovaia (2012), k Am^{-1}, k Am^{-1} (Moreno, Sagnotti et al. 2003)	Ratio of SIRM to susceptibility that provides information on magnetic particle size and composition (Moreno, Sagnotti et al. 2003, Sant'Ovaia 2012)
IRM/ κ		Hanesch (2003)	A/m	Ratio of IRM to susceptibility that gives insight to the class and grain size of the sample (Hanesch 2003)
S ratio		Moreno, Sagnotti et al. (2003), Hanesch (2003), Sant'Ovaia (2012), Davila, Rey et al. (2006)	Dimensionless, Dimensionless, Dimensionless, Dimensionless	Determined from IRM acquisition and backfield magnetization curves that discriminates between high and low coercivity material (Moreno, Sagnotti et al. 2003)

Table 1 (continued)

Chemical

Parameter	Studies used	Units	Description
Median destructive field (MDF$_{ARM}$)	Hansard (2011), Hansard, Maher et al. (2012), Mitchell (2009)	mT, mT, mT	Alternating field required to reduce remanence values to one half of initial value (Moskowitz 1991), indicative of magnetic grain size of ferromagnetic grains (Hansard 2011)
χ$_{ARM}$/SIRM	Hansard (2011), Hansard, Maher et al. (2012), Mitchell (2009)	A, A, A	Ratio indicative of "soft" magnetic grain size of magnetite-like particles affected by presence of "harder" magnetic minerals (Hansard 2011)
Saturation remanence/Saturation magnetization (J$_{rs}$/J$_{s}$)	Jordanova et al. (2003)	Dimensionless	Determined from hysteresis data and calculated

Additional

Parameters	Instrumentation	Studies used	Units	Description
Particle characteristics	Scanning electron microscopy (SEM) with energy dispersive x-ray analyzer (EDXA) (Hanesch 2003, Tomašević, Vukmirović et al. 2005, Dávila, Rey et al. 2006, Mitchell 2009, Tomašević and Aničić 2010, Sawidis, Breuste et al. 2011, Maher, Ahmed et al. 2013) Field emission scanning electron microscope (FE-SEM) (Rodriguez-Germade, Mohamed et al. 2014)	Hanesch (2003), Sawidis, Breuste et al. (2011), Mitchell (2009), Tomašević, Vukmirović et al. (2005), Dávila, Rey et al. (2006), Tomašević and Aničić (2010), Rodriguez-Germade, Mohamed et al. (2014)	μm, μm, nm, μm, μm, μm, μm	Determination of particle sizes and morphologies
Enrichment ratio or pollution factor level	None (but need elemental concentrations or magnetic parameters to calculate)	Maher (2008), Mitchell (2009), Aničić, Spasić et al. (2011), Rodriguez-Germade, Mohamed et al. (2014), Šerbula, Miljkovic et al. (2012), Šerbula, Kalinovic et al. (2013), Šerbula, Radojevic et al. (2014), Tomašević and Aničić (2010), Alagić, Šerbula et al. (2013)	Dimensionless, Dimensionless, Dimensionless, n/a, Dimensionless, Dimensionless, Dimensionless, Dimensionless	May be used for certain magnetic parameters [e.g. mean enrichment ratio of SIRM (roadside: background)] (Maher 2008, Mitchell 2009); metal concentrations in leaves at polluted site compared to metals concentration in leaves at background site (Šerbula, Radojevic et al. 2014)

[a] Values from direct measurements of samples

[b] Calculated values from measurements taken [e.g. HIRM = 0.5 *(SIRM + IRM_300mT)] (Liu, Roberts et al. 2007)

2002); most nutrients are less available when soil pH surpasses 7.5. Ultimately, soil properties are an important consideration for site selection and contribute to reliable elemental source contributions.

Laboratory analytic methods

Various chemical and magnetic analytic methods have been used for elemental compositional analysis of PM on deciduous tree leaves, detailed in Table 1.

Chemical measurements

Chemical methods—including inductively coupled plasma mass spectrometry (ICP-MS) (Sheppard, Hallman et al. 2009; Šućur 2010; Tomašević and Aničić 2010; Tomašević, Aničić et al. 2011; Petrova, Yurukova et al. 2012; Petrova, Yurukova et al. 2014), optical emission spectrometry (ICP-OES) or atomic emission spectrometry (ICP-AES) (Piczak 2003; Davila, Rey et al. 2006; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Simon, Braun et al. 2011; Šerbula, Miljkovic et al. 2012; Šerbula, Kalinovic et al. 2013; Dogan, Unver et al. 2014; Rodriguez-Germade, Mohamed et al. 2014; Šerbula, Radojevic et al. 2014), simultaneous sequential inductively coupled plasma emission spectrophotometry (SIMSEQ) (Samecka-Cymerman, Kolon et al. 2008), and atomic absorption (AA) spectroscopy (Sawidis 1995; Jordanova et al. 2003; Aboal, Fernández et al. 2004; Baycu, Tolunay et al. 2006; Samecka-Cymerman, Kolon et al. 2008; Sant'Ovaia 2012; Šerbula, Miljkovic et al. 2012; Kolon, Samecka-Cymerman et al. 2013)—have been used to quantify trace elemental compositions of multiple media. In comparison to magnetic quantitative methods, advantages of chemical analysis include sensitivity to chemical concentrations at relatively low limits of detection (LOD) and information on a larger suite of elements with more specificity. However, these methods are costly, require technical expertise, irreversibly destroy samples, and require digestion of leaf samples using nitric acid (HNO_3) (Sawidis 1995; Aboal, Fernández et al. 2004; Baycu, Tolunay et al. 2006; Tomašević, Vukmirović et al. 2008), or a combination of HNO_3 and hydrogen peroxide (H_2O_2) (Piczak 2003; Samecka-Cymerman, Kolon et al. 2008; Šućur 2010; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Simon, Braun et al. 2011; Tomašević, Aničić et al. 2011; Petrova, Yurukova et al. 2012; Alagić, Šerbula et al. 2013; Šerbula,

Kalinovic et al. 2013; Petrova, Yurukova et al. 2014; Šerbula, Radojevic et al. 2014) or perchloric acid ($HClO_4$) (Kolon, Samecka-Cymerman et al. 2013; Dogan, Unver et al. 2014) prior to microwave digestion, open-vessel heating, or ashing. Tomašević, Vukmirović et al. (2005, 2008) used differential pulse anodic stripping voltammetry (DPASV) with a hanging mercury drop electrode to determine Pb, Cd, Cu, and Zn post-ashing. The most common digestion method among reviewed studies is use of HNO_3 and addition of H_2O_2 to digest residual material. All digestion reagents used for digestion must be appropriate for trace element analysis (i.e., trace metal grade). For guidance on digestion procedures of environmental samples (including wet and dry), refer to Rüdel, Kösters et al. (2011) or Iso (1972).

Other analytic techniques (e.g., scanning electron microscopy (SEM)) may be required prior to chemical digestion if study hypotheses consider size-resolved PM, as analysis of chemical digests does not provide information on particle size. Notably, Deljanin, Tomašević et al. et al. (2014) estimated three particle size fractions (0.2, 2.5, and 10 μm) on analyzed leaves of *B. pendula*, *A. hippocastanum*, *A. platanoides*, and *T. cordata,* by washing leaves in water then in chloroform. Authors found that *B. pendula* leaves were relatively more efficient in capturing and retaining PM, while *A. hippocastanum* was not far behind, and *A. platanoides* and *T. cordata* were less efficient in retaining PM (Deljanin, Tomašević et al. 2014). However, it was not stated how well each species captured the specific size fractions of PM.

Magnetic measurements

All matters are magnetic but may behave differently in response to applied magnetic fields (Moskowitz 1991). There are five major magnetic groups, which are detailed in Table 2. Environmental magnetic techniques have been increasingly used to investigate sources and temporality of anthropogenic pollution (Liu, Roberts et al. 2012). Magnetic measurements can be derived from urban dust on leaf surfaces, mainly iron oxides from industrial, domestic, and vehicular emissions (Moreno Sagnotti et al. 2003; Davila Rey et al. 2006; Kardel, Wuyts et al. 2013), providing a

semi-quantitative tool for air pollution mapping (Jordanova et al. 2003). Because leaves themselves are insignificantly magnetic, they create minimal interference with magnetic analysis (Maher 2008). Accordingly, magnetic analyses may offer rapid, low-cost, non-destructive methods to determine magnetic particle properties including magnetic grain size and magnetic class, despite the fact that resulting data will not necessarily reflect potential toxicity of certain PM components from a leaf sample (e.g., Pb) (Liu, Roberts et al. 2012). In addition, magnetic properties are sensitive to Fe-containing materials, which are both ubiquitous in environmental systems and sensitive to environmental change (Hatfield 2014).

Magnetic techniques can distinguish between particles produced at different temperatures and redox conditions, providing PM composition and source information (Hansard, Maher et al. 2012). Magnetite-like materials (Fe_3O_4) have been determined to be derived predominately from vehicle-related emissions, while hematite (Fe_2O_3) forms at higher combustion temperatures from industrial sources (e.g., steel production) (Maher 2008; Mitchell 2009; Hansard, Maher et al. 2012; Hofman, Stokkaer et al. 2013), which may depend on the process and type of iron ore used in steel production. Results supporting this come from Hansard (2011), who found hematite concentrations on leaves from industrial areas 100 times greater than roadside leaves. Another study showed that leaves from port areas had higher magnetic measures indicating iron spherules of 5 to 10 μm in diameter, associated with industrial combustion (Davila, Rey et al. 2006).

Magnetic materials in areas of predominantly traffic-derived pollution are typically magnetite (Muxworthy, Matzka et al. 2001), of which iron oxides and hydroxides constitute 10 to 70 % of the approximately 5 to 15 % iron content of urban PM (Dedik, Hoffmann et al. 1992; Weber, Hoffmann et al. 2000). Observed relationships between tree position and roadway suggest associations with engine wear or combustion emissions; Maher (2008) found higher leaf SIRM for leaves from uphill-adjacent trees, lower for leaves from roadside, downhill-adjacent trees, and lowest leaf SIRM for leaves from the distal side of downhill-adjacent trees. Additional factors influencing leaves' magnetic measures include tree distance from roadway and traffic intensity, sampling height (Maher 2008; Power, Worsley et al. 2009; Kardel, Wuyts et al. 2012; Hofman, Stokkaer et al. 2013), fleet composition (Kardel, Wuyts et al. 2012), and street canyonization (Hofman, Stokkaer et al. 2013).

Because magnetic grain size may be inconsistently correlated with ambient particle size (i.e., PM as defined by a regulatory agency such as the US Environmental Protection Agency), this determination warrants supplementary analytic methods for a more lucid interpretation of results. Magnetic grain size refers to the size of the magnetic particle in the sample, while particulate matter is a complex mixture of particles and liquid droplets. Different magnetic grain sizes in a sample can be identified via bivariate plots (e.g., ARM/SIRM), and size of particles in a PM sample should be relatively uniform considering design of the sampling technology. However, PM consists of a number of components in different sizes and shapes (e.g., nitrates and sulfates, organic chemicals, soil, metals) that are considered in its size determination. Unless there is a homogenous sample, "magnetic grain size" and particulate matter ("ambient particle size") may not be used interchangeably. Composition of PM varies by origin or source, and in a study area with multiple pollutant sources contributing to PM (e.g., soil, industrial activity, vehicular emissions), obtaining a strictly homogenous sample is not always likely. Therefore, determination of spatiotemporal patterns of PM using tree leaves as biomonitors requires additional analytic methods, as magnetic techniques identify the largest magnetic anomalies (Liu, Roberts et al. 2012).

Scanning electron microscopy

SEM coupled with energy dispersive x-ray analysis (SEM-EDXA) provides highly resolved leaf surface images for quantification of particle size and elemental composition. This method, however, requires either exhaustive examination by an analyst or appropriate equipment to scan leaf surfaces due to heterogeneity in PM deposition, size distribution, and composition, and thus is time-consuming and/or costly. In addition, the

Table 2 Five major classes of magnetic materials adapted from Moskowitz (1991)

Class	Example(s)	Definition
Diamagnetic	Cd, Cl, Cu	A usually weak fundamental property of all matter, due to non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic materials are composed of atoms with no net magnetic moments, therefore producing a negative magnetization when exposed to a magnetic field.
Paramagnetic	Al, Mg, Na	These materials have a net magnetic moment due to unpaired electrons in partially-filled orbitals, but individual magnetic moments do not interact magnetically, so magnetization is zero when magnetic field removed, but in the presence of a magnetic field, there is partial alignment of atomic magnetic moments in the direction of the field, resulting in a net positive magnetization.
Ferromagnetic	Fe, Co, Ni	These materials are generally highly magnetic because their atomic moments exhibit very strong interactions, produced by electronic exchange forces which results in parallel or antiparallel alignment of atomic moments. There is parallel alignment of magnetic moments resulting in large net magnetization even in absence of magnetic field, therefore enabling maintenance of magnetization in absence of a magnetic field.
Ferrimagnetic	Fe_3O_4	These materials exhibit a type of magnetic ordering, with a structure composed of two magnetic sublattices separated by oxygens. The magnetic moments of the sublattices not equal, resulting in a net magnetic moment, similar to ferromagnetism aside from the magnetic ordering. Ferrimagnetic materials are also able to remain magnetized in the absence of a magnetic field.
Antiferromagnetic	Cr, Fe_2O_3	These materials have well-aligned but opposing magnetic moments, with magnetic forces virtually canceling each other out. They have a net magnetic moment of zero, and are able to remain magnetized in the absence of a magnetic field.

surface of the material being examined could be electrically conductive and coated with electrically conducting material (e.g., Au (Maher 2008), C (Jordanova et al. 2003; Tomašević, Vukmirović et al. 2005; Tomašević and Aničić 2010; Sawidis, Breuste et al. 2011; Rodriguez-Germade, Mohamed et al. 2014), or Pt/Pd), which will compromise a sample if subsequent analysis is required.

Using SEM-EDXA, Maher (2008) examined PM morphology in a subset of leaves, finding spherical clusters ranging from less than 0.5 to 20 μm, comprised mostly of Fe, Si, and Al, and some angular particles 1 to 10 μm diameter, comprised mostly of Fe, S, Al, K, and Ca. Sawidis, Breuste et al. (2011) found that leaf surface analysis revealed particles with variable morphology, structure, and chemical composition as well as relative trapping efficiency for larger particles (20 to 40 μm) on the abaxial (bottom) surface, and small particles (one to 20 μm) on the adaxial (top) surface. Entire leaf surfaces do not always get examined, resulting in a measurement or observation that is not truly representative of the entire leaf sample. To prevent this and to ensure complete analysis, leaf surfaces should be comprehensively examined. Both abaxial and adaxial leaf surfaces should

be considered due to the differential accumulation of variable particle sizes on different surfaces, unless a particular hypothesis warrants only selective investigation of one leaf surface. For example, Tomašević, Vukmirović et al. (2005) used SEM-EDXA but only examined 0.025 % of the leaf surface as a representative sample, despite the fact that SEM showed particles not homogenously distributed across leaf surface; particle density varied from 5000 to 20,000 mm^{-2}. However, authors determined that 50–60 % of analyzed particles on leaf samples were less than 2 μm with spherical shapes and smooth surfaces, occurring singly or agglomerated with other various shaped particles. SEM analysis also revealed that fine and coarse particles were observed around and over the 10 μm stomatal openings, which may contribute to eventual leaf temperature increase and decreased light absorption (Tomašević, Vukmirović et al. 2005). Likewise, Tomašević and Aničić (2010), who also analyzed approximately 0.025 % of each tree species' leaf surfaces (*A. hippocastanum* and *Tilia* spp.), found more particles accumulated on the abaxial leaf surface and around leaf veins. Further, 50–60 % of analyzed particles were less than 2 μm in diameter observed around and over the 10-μm stomatal openings, and were of anthropogenic origin (e.g., soot, fuel oil, coal ash) (Tomašević and Aničić 2010). While this particle characterization is informative, it is time- and resource-consuming, resulting in use of a small surface area examination as a representative sample.

Analytic control leaves

Identifying and obtaining control leaves for analytic calibration (or blank control) can be a challenge, thus few studies have used a "clean" control of the same species. Utilizing a "clean" control from the same species can be problematic, as standard deviations for nutrients among deciduous trees of the same species may range from 8 to 31 % (Luyssaert, Raitio et al. 2002). It is possible that choosing clean control leaves from more than five trees will result in a more representative control. Other studies have compared measured results to generalized approximate concentrations of various trace elements in mature leaf tissue for various species (Kolon, Samecka-Cymerman et al. 2013; Dogan, Unver et al. 2014). However, concentrations for pollution-sensitive or pollution-tolerant species may vary; hence, these values may not be appropriate for comparison. In addition, ranges of trace element concentrations differ among sources cited. For example, Zn concentrations from Kolon, Samecka-Cymerman et al. (2013) describe general mature leaf tissue concentrations of 27 to 150 mg kg^{-1}, while Dogon, Unver et al. (2014) report Zn ranges from 20 to 400 mg kg^{-1} (reported μg g^{-1}). Jordanova et al. (2003) obtained a background leaf magnetic susceptibility measurement using maple tree leaves taken at a nearby mountain's National Reserve (approximately 20 km from study area) 1000 m above sea level. Mitchell (2010) grew glasshouse-grown, "magnetically clean" leaves to adjust for environmental background, then deployed them at background and high-traffic sites for reanalysis. Tomašević, Aničić et al. (2011) found that selecting a control leaf may be challenging due to transport or dispersion of air pollutants of interest, and to environmental conditions on a tree genotype at a location too far from the study domain. Though trees of known age and environmental exposure (e.g., glasshouse-grown trees in a controlled environment) may be ideal for obtaining background elemental concentrations, resources required for this may present additional costs and personnel that are not universally accessible.

Some studies have employed washing, or reference, procedures using distilled, ultrapure, or deionized water (Matzka 1999; Piczak 2003; Aboal, Fernández et al. 2004; Tomašević, Vukmirović et al. 2008; Sheppard, Hallman et al. 2009; Šućur 2010; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Simon, Braun et al. 2011; Sadeghian , Šerbula, Miljkovic et al. 2012; Alagić Šerbula et al. 2013; Hofman, Wuyts et al. 2014), detergents, and/or ultrasonics (Guha and Mitchell 1965; Matzka 1999; Tomašević, Vukmirović et al. 2005; Sadeghian 2012) to clean control leaves for analysis. Few studies washed leaves to examine elemental concentrations solely from uptake via roots or translocation (Šerbula, Kalinovic et al. 2013). Among the reviewed studies, distilled or deionized water was most commonly used for leaf-washing purposes. Matzka (1999) reported that cleaning with water, detergent, and ultrasonics removed 65 to 80 % of magnetic measure—specifically IRM$_{300mT}$—from leaf samples, with residual magnetization attributed to incorporation of dust particles into leaf tissue, imperfect cleaning, or biogenic magnetic contributions. Likewise, upon distinguishing between leaf-encapsulated versus leaf-deposited PM, Hofman, Wuyts et al. (2014) found statistically significant differences between SIRM from washed versus

unwashed leaves, and an average of 38 % of leaf SIRM was attributed to leaf-encapsulated particles following a 2-min hand washing protocol using ultrapure water. Sadeghian (2012) removed 64 to 78 % of leaf magnetization after washing with detergent. When considering trace element removal via washing techniques, Tomašević, Aničić et al. (2011) found that a 3- to 5-s double-rinsing procedure removed significant concentrations of Al, Fe, and Pb from all deciduous species investigated (*A. hippocastanum*, *A. platanoides*, *B. pendula*, and *T. cordata*), but noted significant trace element variation between species from traffic-congested areas (e.g., *A. platanoides* had highest concentrations of Al, Fe, Mn, Pb, Cr, and Cd). In a slightly different approach, Deljanin, Tomašević et al. (2014) presumably divided their leaf samples in half, briefly (3–5 s) soaking half of each leaf sample in bidistilled water twice, leaving the other half unwashed to investigate simulated precipitation effects on leaf Pb concentrations. Authors found that approximately 30 % of Pb was removed from leaf surfaces. Tomašević, Antanasijević et al. (2013) employed a similar approach. Authors also found that Pb concentrations were higher in unwashed leaf samples, and that there were similar isotopic ratios (Pb) among unwashed leaf samples, concluding that the deposited fraction of Pb was from a single dominant source since the previous rainfall event (Deljanin, Tomašević et al. 2014).

The variety of leaf washing procedures can affect PM constituent determination. Therefore, application of a standard washing technique is necessary for data comparison across different studies, though published data usually lack the details of duration and type of washing media (Deljanin, Tomašević et al. 2014). Ataabadi (2012) provide guidance on leaf washing procedures and specifically assess leaf washing procedures for determination of airborne metal concentrations. Authors suggest that the washing agent depends on study hypothesis, species (i.e., deciduous vs. evergreen), leaf structure (e.g., leaf type, cuticle thickness, roughness), and properties of airborne metal concentrations (e.g., solubility), and determined distilled water most appropriate washing media for deciduous species, as it is safe, cost-effective, and efficient. A 10-min washing period was determined to be suitable, based on comparisons among 5-, 10-, 15-, and 30-min leaf washings. Compared to unwashed leaves, however, the washing treatment varied between metals; Al, Fe, and Ni concentrations were greatly reduced, while washing had no significant effect for Mn, Zn, and Cu removal from leaf surfaces (Ataabadi 2012). Considering that Deljanin, Tomašević et al. (2014) determined a short (i.e., 3–5 s) washing procedure was effective at eliminating a fraction of Pb from leaf surfaces emphasizes the variability in retention rates among different metals on tree leaf surfaces. To date, a standard washing procedure for dry and wet deposited metals for PM constituent determination from leaves of deciduous tree species has not been identified.

Nutrient uptake and integration varies with species and nutrient availability, and trees can survive only within distinct ranges of nutrient concentrations (Baycu, Tolunay et al. 2006), which vary over the vegetative cycle (Guha and Mitchell 1965, Guha and Mitchell 1966, Tomašević, Vukmirović et al. 2008). Thus, determining the leaf's "chemical fingerprint" may help disentangle inherent elemental concentrations from anthropogenic contributions (Tomašević, Vukmirović et al. 2008), if this "fingerprint" is not impossibly variable. Despite the fact that one study dismissed leaves as insignificantly magnetic (Maher 2008), it has been suggested that in unpolluted leaves, Fe exists in the form of phytoferritin with a central cavity composed of a mixture of iron oxides including ferrihydrites and magnetite (McClean and Kean 1993; Størmer and Wielgolaski 2010). Ferrihydrite is paramagnetic, but magnetite is ferrimagnetic, which may to some extent contribute to or confound interpretation of magnetic results if not considered. Despite the difficulties in obtaining a control leaf or leaves, one should be utilized for comparison against leaf samples from sampled (hypothesized polluted) areas or to potentially blank-correct sampled leaves.

Effects of weather, precipitation, and moisture

Leaves are not sheltered from weather, which may result in sample loss or reduced collection efficiency, and may vary with leaf position on the tree or irregular surface structure (Rodriguez-Germade, Mohamed et al. 2014). The net effect of precipitation on leaf surface PM integrity is unclear (Muxworthy, Matzka et al. 2001), and study designs require attention to variation in moisture conditions. Collecting leaves before and after rainfall may reveal precipitation-mediated changes in

concentrations. Kardel (2011) observed limited rain-induced wash-off, and increased SIRM of PM concentrations over the growing season in two species, possibly from PM accumulation in the leaf tissue. Similarly, Hofman, Wuyts et al. (2014) found limited effect of rainfall on leaf SIRM during a one week sampling period. Others reported decreased leaf SIRM and metal concentrations, SIRM, and IRM_{300mT} of 5 to 30 % (Maher 2008), 12 to 64 % (Mitchell 2009), and 28 % (Matzka 1999) after a rainstorm, respectively, while Moreno, Sagnotti et al. (2003) observed no significant change in magnetic measures—specifically magnetic susceptibility—after rainfall.

Other studies examined precipitation effects using leaf washing (Matzka 1999: Piczak 2003; Aboal, Fernández et al. 2004; Šućur 2010; Aničić, Spasić et al. 2011) or leaching procedures (Davila, Rey et al. 2006; Maher 2008; Rodriguez-Germade, Mohamed et al. 2014), though the process may imperfectly represent precipitation effects (Tomašević, Vukmirović et al. 2008). For example, Davila, Rey et al. (2006) reported leaf samples with higher SIRM measures retaining up to 20 % of initial measures post-leaching; those with lower initial SIRM had post-leaching SIRM close to instrument LOD. Rodríguez-Germade, Mohamed et al.'s (2014) procedure removed 69 to 97 % of Al, Cu, Fe, Mn, and Zn, and Maher's (2008) removed approximately 75 % of initial SIRM. Light precipitation events (e.g., drizzle) consisting of minute droplets of water may accumulate on leaf surfaces and contribute to metal content, while heavier precipitation events and associated windy conditions may wash leaf surfaces. Organizing sampling around monitored weather patterns may result in more interpretable results. If impossible, obtaining rainfall and wind data from local or regional weather monitoring stations (e.g., National Oceanic and Atmospheric Administration (NOAA) land-based weather station) or keeping a data log of rainfall events and wind conditions during sampling campaigns can be used to account for these potential variables during interpretation.

Leaf moisture content can vary across the growing cycle (Tomašević, Vukmirović et al. 2008) and with soil moisture status; therefore, several leaf drying procedures have been developed to standardize the analysis of dry mass (Sawidis 1995; Jordanova et al. 2003; Piczak 2003; Aboal, Fernández et al. 2004; Samecka-Cymerman, Kolon et al. 2008; Tomašević, Vukmirović et al. 2008; Power, Worsley et al. 2009; Sheppard,

Hallman et al. 2009; Šućur 2010; Tomašević and Aničić 2010; Aničić, Spasić et al. 2011; Kardel 2011; Tomašević Aničić et al. 2011; Petrova, Yurukova et al. 2012; Sant'Ovaia 2012; Šerbula, Miljkovic et al. 2012; Alagić, Šerbula et al. 2013; Hofman, Stokkaer et al. 2013; Kolon, Samecka-Cymerman et al. 2013; Šerbula, Kalinovic et al. 2013; Dogan, Unver et al. 2014; Petrova, Yurukova et al. 2014; Rodriguez-Germade, Mohamed et al. 2014; Šerbula, Radojevic et al. 2014). Accordingly, studies which did not dry leaves, but instead stored samples in a refrigerator (Sawidis 1995; Davila, Rey et al. 2006; Mitchell 2009; Mitchell 2010; Hansard 2011; Simon, Braun et al. 2011; Hansard, Maher et al. 2012; Dogan, Unver et al. 2014; Rodriguez-Germade, Mohamed et al. 2014) or freezer (Aboal, Fernández et al. 2004) until analysis, may not be directly comparable to dry leaves. An additional option not included in reviewed studies is freeze-drying, which may increase comparability with other leaf drying procedures.

Validation against PM measures from sampling instrumentation and/or modeling

Validating leaf magnetic and elemental measures against traditional air monitoring data, or additional active sampling, is critical for understanding the utility of tree leaves as adequate sampling media for environmental exposure studies, though not all studies reviewed here include validation. For example, Dogan, Unver et al. (2014) compared leaf versus bark samples across different locations in the city center of Artvin, Turkey in order to assess utility of leaves versus bark regarding detection of heavy metal air pollution. Šerbula, Kalinovic et al. (2013) and Šerbula, Radojevic et al. (2014) sampled and analyzed leaves, branches, roots, and soil to determine the degree of elemental uptake via soil, roots, translocation, and atmospheric deposition.

However, multiple studies reported positive correlations between leaf-based magnetic measures and atmospheric PM measurements (Mitchell 2009; Power, Worsley et al. 2009; Hansard 2011). Power, Worsley et al. (2009) used a hand-held P-Trak Ultrafine Particle Counter to measure $PM_{1.0}$ concentrations at each leaf sampling site during peak traffic hours, reporting positive correlations ($R^2 > 0.77$) between $PM_{1.0}$ and χ_{LF} ($R^2 = 0.60$, $p > 0.05$), ARM ($R^2 = 0.75, p > 0.05$), and SIRM ($R^2 = 0.78$, $p < 0.05$) of roadside *Tilia europaea* leaves, and between $PM_{1.0}$ and χ_{LF} ($R^2 = 0.79$,

$p < 0.05$), ARM ($R^2 = 0.94$, $p < 0.01$), and SIRM ($R^2 = 0.96$, $p < 0.01$) of roadside *A. pseudoplatanus* leaves, with higher $PM_{1.0}$ concentrations near roadways with more idling vehicles. Hansard (2011) co-located SidePak AM510 personal aerosol monitors for coarse PM_{10} (particulate matter with aerodynamic diameter less than 10 μm) with sampled trees, reporting positive associations with leaf SIRM ($R^2 = 0.71$, $p = 0.01$). In the same study, comparisons were made between leaf-derived PM_{10} estimates and Gaussian plume dispersion model results for a nearby industrial site's main stack; model results underestimated ambient PM_{10} which is expected for single-source models that may omit other significant contributions (e.g., fugitive dust), but spatial patterns of leaf SIRM corresponded with monthly-averaged prevailing wind direction from the industrial site (Hansard 2011). Mitchell (2009) collected 1-h PM_{10} samples at leaf sampling sites using SKC Leyland Legacy personal monitors with magnetically-clean Teflon® filters. Despite different sampling intervals, filter samples correlated strongly with mean leaf SIRM ($R^2 = 0.80$, $p = 0.01$). Leaf magnetic measures and filters revealed similar ranges of particle sizes, morphologies, and compositions, with most particles in the 0.1- to 1 μm-diameter range. Elemental analysis revealed high Fe concentrations in submicrometre particles, and higher concentrations of Al and Si in larger (≤5 μm) angular particles. The authors further compared mean PM_{10} leaf measures with dispersion model predictions, reporting a correlation of $r = 0.60$ ($p = 0.01$) (Mitchell 2009). SEM-EDXA showed that major PM elemental contributions from most to less abundant were $C > O > Fe > Ti > Si > Ca > Al > Na > K > Cl > Mg$. Finer particles (<200 nm) observed were smooth and Fe-rich with spherical or semi-spherical morphology and were determined to greatly contribute to SIRM from television swabs and tree leaves, as opposed to the irregular-shaped and sized coarse particles (approximately 1 to 10 μm).

In contrast, Hofman, Wuyts et al. (2014) found no relationship between weekly leaf SIRM, and daily and weekly averaged PM_{10} and $PM_{2.5}$ concentrations, except for their first five daily sampling events in June (washed leaf SIRM and PM_{10} $R^2 = 0.96$, unwashed $R^2 = 0.99$; washed leaf SIRM and $PM_{2.5}$ $R^2 = 0.94$, unwashed $R^2 = 0.81$). However, authors also hypothesized from this finding that leaf-encapsulated PM fixed inside the leaf tissue represents a less dynamic fraction unaffected by wash-off or resuspension, and supported by higher statistically significant correlations between washed leaf SIRM and cumulative (i.e., entire in-leaf season) daily PM_{10} ($R^2 = 0.87$) and $PM_{2.5}$ ($R^2 = 0.87$) concentrations (Hofman, Wuyts et al. 2014). Additionally, Hofman, Wuyts et al. (2014) were unable to determine whether or not SIRM has utility for measuring weekly variation in cumulative PM concentrations. Nonetheless, as is evident from these findings, the strong correlations between leaf and validated measures (either via sampling or modeling) have demonstrated the utility of tree leaves for magnetic biomonitoring.

Observed associations between sources and measures of concentration or composition

Despite challenges in using tree leaves as biomonitors of PM pollution, meaningful associations between leaf-derived measures and local emissions sources have been observed. Davila, Rey et al. (2006) identified higher SIRM for leaf samples from urban areas with higher traffic density and spherical iron particles (five to 10 μm in diameter) from combustion sources using magnetic methods. Kardel, Wuyts et al. (2012) found that leaf SIRM decreased with increasing distance from nearest road, and increased with higher traffic intensity and tram frequency in the study domain. In an area with heavy metal pollution from a smelting factory, Jordanova et al. (2003) found enhanced magnetic susceptibility values and concentrations of Pb, Cu, and Zn for leaves closer to the smelting factory compared to the background site; the smelting process in these particular kilns uses Cu, Mn, Si, Fe, Ni, Zn, Pb, and Ti.

Using chemical analysis, Šerbula, Radojevic et al. (2014) found higher concentrations of Cu, Mn, and Zn in birch leaves in the vicinity of a copper smelter compared to those at the background site. Similarly, Šerbula, Kalinovic et al. (2013) found Cu concentrations higher than those toxic to aerial parts of plants (i.e., >20 μg/g) in areas closer to the source—a copper smelter—and a decrease in leaf Pb concentrations with increasing distance from the source. Petrova, Yurukova et al. (2012) found statistically significant positive correlations between *A. hippocastanum* leaf Cr and V concentrations, attributed to vehicle emissions from urban traffic.

Baycu, Tolunay et al. (2006) found higher Pb concentrations in leaves from roadside sites. Similarly, Tomašević, Vukmirovic et al. (2008) hypothesized the source of Pb from leaf samples to be from traffic emissions, as leaded gasoline was the predominant fuel used in their sampling domain, and Sawidis, Breuste et al. (2011) found that leaves from city centers had higher concentrations of metals associated with vehicular and industrial activities (Cr, Cu, Fe, Pb). Using principal components analysis (PCA), Šerbula, Radojevic et al. (2014) found a high positive correlation of Cu and Pb from leaves sampled at sites near a copper smelter, indicating anthropogenic origin. A traffic-related influence was also concluded by Tomašević, Vukmirović et al. (2005), who observed fuel oil rich particles containing Al, Si, Ca, Ni, Fe, V, and Pb, with a lesser influence from local industrial sources and soil resuspension, on leaf samples analyzed via SEM-EDXA. Simon, Braun et al. (2011) found that leaf wash (solution derived from leaf-washing procedures) from urban areas had higher concentrations of Na, Ba, Sr, Pb, Fe, Se, Al, Cu, Co, Mg, As, and Ca, and leaves from urban areas had higher concentrations of Zn, Mn, Mg, Cu, Ca, P, K, Cd, Ba, and Li, both associated with vehicular and industrial activities.

In an effort to parse out Pb contributions from different sources, Deljanin, Tomašević et al. (2014) and Tomašević, Antanasijević et al. (2013) used stable Pb isotope ratios (radiogenic ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) and Pb concentrations to infer source information, determine an isotopic fingerprint from their leaf samples, and observe trends over time. Because foliar uptake of Pb is considered the dominant pathway via atmospheric deposition, source attribution is relatively more straightforward. Highest leaf Pb concentrations were found at the high-traffic site for both washed and unwashed leaves, and similar isotopic (Pb) ratios were found in unwashed leaf samples in the urban area of Belgrade, Serbia (Deljanin, Tomašević et al. 2014). Tomašević, Antanasijević et al. (2013) found that ^{206}Pb/^{207}Pb were higher earlier (1.135 in May) compared to later (1.126 in September) in the vegetative season and that leaf Pb concentrations decreased over the multi-year sampling campaign, aligning with the phasing out of leaded gasoline use. For comparison, the ^{206}Pb/^{207}Pb isotopic composition of gasoline and vehicular exhaust reported from some European countries were within the range of 1.059–1.132 (Tomašević, Antanasijević et al. 2013). One of Deljanin, Tomašević et al.'s (2014) sampling sites revealed an additional source of Pb—in addition to traffic—due to more scattered isotopic ratios among washed leaves, hypothesized as either originating from localized fuel oil and natural gas heating units proximal to the sampling site, or from Pb contributions from a downwind oil refinery referring to data from another study. Another site revealed relatively lower isotopic ratios, but Pb contribution from a thermal power plant approximately 18 mi (30 km) away. Authors also investigated isotopic ratios in washed leaves over time (2002–2009), finding that Pb isotopic ratios from 2002 to 2006 were enriched with additives from Australian ores, similar to isotopic ratios of Australian particles. In 2006, additives from Chinese ores enriched gasoline, reflected in the Pb isotopic ratios from leaves sampled in 2009 comparable to isotopic ratios of Chinese particles (Tomašević, Antanasijević et al. 2013, Deljanin, Tomašević et al. 2014). In general, there are few studies analyzing isotopic ratios from tree leaves, leaving little inter-study comparison of data. However, from these results, it appears that meaningful associations have been shown between sources and measures of concentration and composition using magnetic and chemical methods.

Conclusions

There is a growing need for cost-effective methods to capture and identify sources of intraurban spatial variation in fine particle concentration and composition. Deciduous tree leaves exposed throughout the leaf growing season may offer a low-cost means of collecting stationary seasonal PM samples across urban areas. Some characteristics of deciduous tree leaves, such as size and surface roughness, can influence the rate of particle deposition and improve particulate capture. Use of pollutant-tolerant, robust species may improve ability to capture full spatial variation in pollutant concentration and composition throughout an urban area, but ultimately the most abundant tree species with high PM collection efficiencies may serve as the ideal biomonitor. Additionally, a multi-year

investigation of biomonitoring for urban PM using a single species should be explored to ensure spatiotemporal consistency.

Magnetic and chemical leaf-based analyses require further validation against actively-sampled, co-located or modeled PM concentrations to derive location or source-specific associations for use in human exposure and epidemiology studies. A multiple-technique approach, such as coupled magnetic and microscopy analyses (Sagnotti, Taddeucci et al. 2009), could be employed for better characterization of pollutants—depending on hypothesis–and source characterization (Davila, Rey et al. 2006) for leaf-based methods to be practical in exposure assessment. Thus, there are unique benefits to using deciduous tree leaves as biomonitors for characterizing spatially-resolved variation in ambient PM or for source-specific investigations, though methods refinement is needed to reduce uncertainties for general application and potential use in exposure and epidemiology studies.

AA, atomic absorption spectroscopy; Al, aluminum; As, arsenic; Au, gold; Ba, barium; C, carbon; Ca, calcium; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; DPASV, differential pulse anodic stripping voltammetry; Fe, iron; Fe_2O_3, hematite; Fe_3O_4, magnetite; GPS, global positioning system; H_2O_2, hydrogen peroxide; ha, hectare; HNO_3, nitric acid; $HNO_3 + HCl$, nitric acid + hydrochloric acid (aqua regia); IAEA, International Atomic Energy Agency; ICP-AES, inductively-coupled plasma atomic emission spectrometry; ICP-MS, inductively-coupled plasma mass spectrometry; ICP-OES, inductively-coupled plasma optical emission spectrometry; K, potassium; km, kilometer; Li, lithium; LOD, limit of detection; m, meter; Mg, magnesium; mm, millimeter; Mn, manganese; Na, sodium; P, phosphorus; Pb, lead; Pd, palladium; PM, particulate matter; $PM_{1.0}$, particulate matter with aerodynamic diameter less than 1.0 μm; $PM_{2.5}$, particulate matter with aerodynamic diameter less than 2.5 μm; PM_{10}, particulate matter with aerodynamic diameter less than 10 μm; PCA, principal components analysis; Pt, platinum; S, sulfur; Se, selenium; SEM-EDXA, scanning electron microscope with energy dispersive x-ray analysis; Si, silicon; Sr, strontium; Ti, titanium; μm, micrometer; Zn, zinc;.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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