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Leaves from twenty-three deciduous tree species and five conifer species were collected within a limited geographic range (1 km radius) and evaluated for possible application of scanning electron microscopy and X-ray microanalysis techniques of individual particle analysis (IPA). The goal was to identify tree species with leaves suitable for the automated characterization of aerosol particles deposited on their adaxial surfaces. Evaluations considered morphology of the leaf surface, ability of the preparations to withstand the high vacuum environment of the IPA equipment and potential for X-ray background interference. Eleven candidate species were tested under auto-run conditions (unattended analyses); the geometric mean particle size, mass median diameter and aerosol deposit mass loading are reported. Particle size, particle population per unit area and mass loading were log normally distributed. Variability in mass loading for the co-located species was about the same as within-leaf and between-leaf mass loading determined for linden leaves, and was inversely related to the area of leaf analyzed. Results for computer automated scanning electron microscopy of individual particles demonstrate the feasibility of monitoring particle assemblages directly on leaf surfaces.

Key words: computer automated scanning electron microscopy, individual particle analysis, tree leaves

INTRODUCTION

Vegetative surfaces provide an enormous sink for both gaseous and particulate atmospheric pollutants (Hosker and Lindberg, 1982; Calamari *et al.*, 1991; Simonich and Hites, 1995). Understanding the dynamics of particle interception and retention has important implications for agricultural sciences (e.g., foliar application of pesticides); for evaluating the effects of air pollutants on forest reserves (Smith, 1974; Krivan *et al.*, 1987; Mossnang, 1991); and as an aid for planners, managers and policy analysts in the development of air quality strategies that include urban vegetation. Atmospheric pollutant attenuation by tree leaves in urban environments may be advantageous from a human health perspective (Smith, 1977), and can be significant in magnitude (Nowak, 1994; Nowak, *et al.*, 1997).

A variety of techniques have been employed to estimate the efficiency of particulate matter interception by tree leaves. Some indirect methods compare dustfall measurements in collectors deployed beneath tree canopies with those in adjacent open spaces, ascribing the difference to the influence of the vegetation (Dochinger, 1980; Beier and Gundersen, 1989). Other indirect approaches rely on atmospheric aerosol monitoring, meteorological measurements and the use of predictive deposition velocity models (Bache, 1979; Wiman *et al.*, 1985). Direct measurements have been more commonly applied, usually by washing the particulate matter from the leaves for subsequent characterization

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(Brabec *et al.*, 1981; Yunus *et al.*, 1985; Lindberg and Lovett, 1985; Dasch, 1987; Pinder and McLeod, 1989; Simmleit *et al.*, 1989). Washing with organic solvents to remove both the particulate material and the epicuticular wax is the method of choice for the study of toxic, semi-volatile organic substances such as poly-chlorinated biphenyls (PCB's) and polynuclear aromatic hydrocarbons (PAH's). Most such investigations, but not all (Thomas *et al.*, 1985), have been restricted to coniferous species (Eriksson *et al.*, 1989; Jensen *et al.*, 1992; Franich *et al.*, 1993; Kylln *et al.*, 1994).

Direct measurement techniques, which could be described as *in situ* applications, have, in general, been microscopy-based methods; a notable exception is the work of Shanley (1989) who employed *in situ* washing/leaching in the study of dry deposition to spruce foliage. Both Davidson and Chu (1981) and Coe and Lindberg (1987) studied particles on leaf surfaces directly in the scanning electron microscope (SEM), providing semi-quantitative information on particle size distributions and mass loading. Both studies, however, encompassed limited numbers of leaf samples and small populations of individual particle characterizations. Significantly larger particle populations were characterized by Fortmann (1982), and Fortmann and Johnson (1984a, 1984b), using computer assisted SEM methods. Their studies examined the dynamics of particle interception and retention by *Taxus* sp. needles in association with atmospheric precipitation events.

The individual particle analysis (IPA) capabilities of automated SEM systems offer some significant advantages in comparison with other direct methods of quantifying tree leaf attenuation of atmospheric particles. First, information on size, shape and elemental composition can be provided for hundreds of individual particles in each specimen examined for each hour of analytical time. This approach allows for a detailed description of the size distribution and population enumeration of many different particle types simultaneously. Second, with suitable particle classification algorithms it is possible to estimate the particle-type mass loading directly on the leaf surface for whatever size range is of interest. Third, this information on particle assemblage characteristics can be obtained from specimens of small size simplifying the logistics of specimen archiving and providing for smaller scale resolution studies of inter- and intra- leaf variability.

The present work examines the application of such computer automated IPA methods to a variety of tree leaves, focusing on the physical attributes of the particle deposits. Specimens from 23 deciduous tree species common to the Northeastern United States but with wide geographic distribution, along with 5 coniferous species, were included in the initial study (Table 1). For deciduous trees, two main objectives were to identify candidate species appropriate for direct application of the automated (unattended) IPA techniques, and to examine the spatial variability of particle deposits on those species. The overall goal was to determine whether suitable deciduous trees are commonly available for this type of environmental analysis. These feasibility studies provide information for the design of sampling and analysis programs incorporating the characterization of particle deposits on tree leaf surfaces.

METHODS

Sample collection and preparation

Twenty-five specimens for evaluation (Table 1) were collected in Syracuse, NY, on or near the campus of the SUNY College of Environmental Science and Forestry during the second week of October 1996. These trees were all growing within a 1 square km area, and are termed the "Cemetery Samples". Two additional species (linden, ponderosa pine) were added during 1997, and samples of Jeffrey pine were obtained from the Lake Tahoe basin in February of 1998. Samples of deciduous leaves were cut with a new razor blade from the mid-section of each leaf about half way between the central vein and the leaf edge. Processing was carried out in a laminar-flow clean bench. The roughly 6 x 8 mm fresh (adaxial only) leaf sections were affixed to 1 cm graphite pin mount SEM stubs using colloidal graphite in alcohol. Larger (2 cm square) specimens were prepared using white glue (Elmer's) to affix the samples to 2.5 cm diameter carbon disks. This stronger adhesive was necessary to maintain a flat (focused) sample when long analysis times were required in the high vacuum environment of the SEM. Whole conifer needles were treated in the same fashion, except for ponderosa pine, where sections were used. Specimens were coated with carbon in a Kinney SC2 high vacuum evaporator prior to individual particle analysis.

Automated SEM individual particle analyses

Characterizations of the aerosol particles on the leaf surfaces were conducted with an Advanced Research Instruments (ARI, Boulder, CO) AutoSEM-1 system interfaced to the ETEC AutoScan SEM using an ARI X-ray spectrometer (KEVEX detector) and an ARI back scatter electron detector. All

Table 1. List of tree species sampled for evaluation. All specimens, except those noted, were obtained during the second week of October, 1996. ARI = IPA characterization with Advanced Research Instruments AutoSEM 1, for x-ray background (bkgd), particle sizing, mass loading (ML) determinations. Auto = unattended analysis mode.

Common Name	Species	Evaluation history	Auto
Apple	*Malus* sp.	ARI: bkgd + ML	yes
Butternut	*Juglans cinerea*	ARI: bkgd + ML	yes
Catalpa	*Catalpa speciosa*	visual examination only	
Cherry	*Prunus serotina*	ARI: bkgd + ML	yes
Cottonwood	*Populus x deltoides*	ARI: bkgd + ML	yes
Dogwood	*Cornus* sp.	ARI: bkgd	
Douglas Fir	*Pseudotsuga menziesii*	ARI: bkgd + ML	
Elm	*Ulmus americana*	ARI: bkgd	
Ginkgo	*Ginkgo biloba*	ARI: bkgd	
Hackberry	*Celtis occidentalis*	ARI: bkgd	
Hawthorne	*Crataegus mollis*	ARI: bkgd	
Honey Locust	*Gleditsia triacanthos*	ARI: bkgd	
Horse Chestnut	*Aesculus hippocastanum*	ARI: bkgd	
Jeffrey Pine *	*Pinus jeffreyi*	ARI: bkgd	
Lilac	*Syringa vulgaris*	ARI: bkgd + ML	yes
Linden **	*Tilia x euchlora*	ARI: bkgd + ML	yes
Magnolia	*Magnolia x soulangeana*	ARI: bkgd	
Norway Spruce	*Picea abies*	ARI: bkgd	
Oak	*Quercus rubra*	ARI: bkgd + ML	yes
Pear	*Pyrus* sp.	ARI: bkgd + ML	yes
Ponderosa Pine ***	*Pinus ponderosa*	ARI: bkgd + ML	
Red Maple	*Acer rubrum*	ARI: bkgd + ML	yes
Sugar Maple	*Acer saccharum*	ARI: bkgd + ML	yes
Sycamore	*Platanus occidentalis*	ARI:discontinued	
Taxus	*Taxus* sp.	ARI: bkgd + ML	
White Birch ****	*Betula papyrifera*	ARI: bkgd + ML	yes
Willow	*Salix babylonica*	visual examination only	
Zelkova	*Zelkova serrata*	visual examination only	

* From Lake Tahoe Basin, sampled February 1998.
** Sampled in several locations in Syracuse, on several dates in 1997.
*** Sampled 8/11/97.
**** Sampled 7/16/97.

analyses were carried out at a magnification of 150 times (field of view 600 μm by 600 μm), using an accelerating voltage of 20 kV. The minimum search point density used by the image analyzer was 0.293 μm; data for particle size distributions smaller than this are incomplete. The ARI system was fully automated for unattended analysis. When 12-field (4 x 3) unattended runs were conducted, analysis times varied between 45 and 90 minutes depending upon the number of particles characterized. X-ray background characteristics of the leaf samples were determined at a magnification of 500 times and a reduced field margin so that a raster scan of particle free areas measuring 35 μm x 35 μm was analyzed.

Mass Loading Calculations and Washing Experiments

Particle volume was approximated from measures of individual feature width and length assuming the particle was a prolate spheroid rotated around its major axis. The average specific gravity of particles was assumed to be 2.5 g cm^{-3} (Coe and Lindberg, 1987). The PM-10 (particle mass contributed by features with aerodynamic diameter less than or equal to 10 μm) loading was computed by assuming that the aerodynamic diameter of a particle was equal to its optical diameter times the square root of its specific gravity. Thus the PM-10 loading estimate was derived

Table 2. Potential for X-ray contamination of individual particle characterizations on leaf surfaces, ranked by net X-ray count rate for various tree species. Net X-ray counts from 4 seconds of live time acquisition at 20 kV are the average of 10, particle-free leaf surface analyses, each covering an area of 1225 square micrometers. Average X-ray counts from the leaf surface for the specified elemental regions of interest are ranked* from 'nil' (<100) to 'severe' (>1000).

Species	Counts	Al	Si	P	S	Cl	K	Ca	Fe
Taxus	163	-	-	-	-	-	-	-	-
D. Fir	182	-	-	-	-	-	-	-	-
Ponderosa	203	-	-	-	-	-	-	-	-
N. Spruce	203	-	-	-	-	-	-	-	-
Oak	238	-	-	-	-	-	-	-	-
Hawthorne	351	-	-	-	-	-	-	1	-
Ginkgo	368	-	-	-	-	-	-	1	-
Jeffrey Pine	427	-	-	-	-	-	-	-	-
Butternut	455	-	1	-	-	-	-	1	-
Linden	460	-	-	-	-	-	1	2	-
Cherry	465	-	-	-	-	-	-	2	-
Pear	480	-	-	-	-	-	1	2	-
H. Locust	586	-	-	-	-	-	-	2	-
Apple	614	-	-	-	-	-	2	1	-
W. Birch	614	-	-	-	-	-	-	2	-
H. Chestnut	709	-	-	-	-	-	2	1	-
S. Maple	835	-	3	-	-	-	-	1	-
Lilac	926	-	-	-	-	1	3	1	-
Hackbry.	1056	-	-	-	-	1	2	3	-
Cottonwd.	1092	-	3	-	-	-	1	2	-
Dogwood	1613	-	-	-	-	1	1	4	-
Magnolia	2025	-	4	-	-	-	1	2	-
R. Maple	2281	-	4	-	-	-	-	-	-
Elm	2911	-	4	-	-	-	1	3	-

*Rankings: <100: nil (-); 100-200: low (1); 200-400: med (2); 400-1000: high (3); >1000: severe (4)

from the summation of individual particle 'mass' for features with optical diameters less than 6.32 μm. The mass median diameter (geometric mass mean diameter, D_gM) of the particle deposits on the leaves was estimated as:

$$\text{Log } D_gM = \Sigma m_j \text{ Log } d_j / M \quad (1)$$

where m_j is the estimated mass of the individual particle, d_j is its diameter and M is the total particle mass. In order to indicate the bias a few large particles might bring to the estimate of mass median diameter, results were tabulated after truncation of the largest particles. The observations for each sample were ranked by ascending particle mass and computations were made ignoring the largest 0.1%, 0.5% or 1.0% of the distribution. The resulting mass median diameter estimates apply to the smallest 99.9%, 99.5% or 99.0% of the analyzed populations in each sample.

To provide a comparison between the calculated particle mass loading and gravimetric mass determinations, washing experiments were performed for the ponderosa pine specimens. In three separate trials, 50 needles (about 6 g) were washed for 15-20 seconds with chloroform (Simmleit *et al.*, 1989). The solution was filtered through glass fiber filters for gravimetric determination of the aerosol particle mass. Surface area of the needles was approximated as a rhomboidal prism using measured needle length, width and thickness.

RESULTS AND DISCUSSION

Species and Surface Suitability

Four of the 28 species analyzed (Table 1) to determine their suitability for SEM particle characterizations were eliminated from consideration early in the study. About half of the features imaged on the sycamore specimen were calcium and sulfur rich particulate inclusions within the leaf structure, from underneath the epicuticular wax layer. These were not evident from visual examination of the leaf surface using the ordinary secondary electron signal, but were located with the back scattered electron signal used in the image analysis procedures.

Three other samples were eliminated on the basis of leaf surface morphology considerations. Zelkova and catalpa have a complex, fibrous appearance making isolation of the aerosol particle images difficult to perform accurately. The willow specimen exhibited substantial 'peel-back' of the epicuticular wax (EW) layer after carbon coating and desiccation. These same kinds of morphological considerations are generally applicable to the abaxial leaf surface where the imaging procedures are frequently unable to distinguish between aerosol particles and structures that are part of the leaf surface.

X-ray Contamination from the Leaf Substrate

High X-ray background from features within the leaf structure may mean they are imaged in back scatter electron mode and counted as being on the leaf surface instead of below it. Thus, the potential for X-ray 'contamination' is an important parameter in the evaluation of different leaf surfaces for individual particle analysis feasibility. Table 2 shows the comparative results for 24 different leaf species all analyzed under the same SEM operating conditions. Results are ranked by X-ray count rate and semi-quantitative indications of specific elemental interferences are tabulated. These should be viewed as preliminary evaluations because of the small sample size. Variation within species is expected with season and with location (soil chemistry).

Ranking of Species Suitability for Automated IPA

Criteria used to establish the suitability of the specimens for automated individual particle analysis included surface smoothness and morphology, viability of the specimen mountings and preparation, and the absence of X-ray interference or other imaging artifacts. Table 3 summarizes the categories developed for this ranking. Species listed in Category I were judged optimum for the automated IPA techniques, while those in Category Ia were physically suitable but showed some degree of X-ray background interference. To maintain focus between adjacent fields of view during automated analyses, the specimen surface needed to be as smooth and flat as possible. Species in Category II (Table 3) did not meet these criteria as they developed cracks on drying, exhibited 'peel back' of the epicuticular wax or suffered failure of the mounting adhesive. Entries for deciduous species under Category III (Table 3) reflect analysis difficulties associated with the presence of trichomes. In many cases, however, visual selection of fields of view by the operator can allow semi-automated particle characterizations to be carried out.

Table 3. Categories of specimen suitability for automated Individual Particle Analysis characterizations (unattended analysis).

Category I. Auto runs tested; no specimen preparation failures. Chemical interferences and imaging artifacts negligible.
Apple, Butternut, Cherry, Linden, Oak, White Birch
Category Ia. Auto runs tested; no specimen preparations failures. Chemical interferences or imaging artifacts possible.
Cottonwood (B), Lilac (B), Pear (B,V), Red Maple (B), Sugar Maple (B)
Category II. Auto runs not tested. Leaf surface characteristics suitable, but specimen mounts and preparations require development.
Ginkgo (C), Honey Locust (P), Horse Chestnut (M), Magnolia (B, P)
Category III. Auto runs not possible due to surface obstructions or morphology. Leaf surface suitable for IPA with operator-selected fields of view.
Douglas Fir (F), Norway Spruce (F), Ponderosa Pine (F), Jeffrey Pine (F), Dogwood (T), Elm (T), Hackberry (T, M), Hawthorne (T,V)

Notes: B= possible chemical background; M= mounting failures; S= surface characteristics not ideal; C= cracks after mounding; P= epicuticular wax peel back; T= trichomes obstructing some fields; V= vein structure obstructing some fields; F= morphological form not optimum for unattended analysis

Physical Characteristics of Particle Assemblages on the Cemetery Leaves

Particle size distribution and mass loading data were collected using auto runs (unattended analysis)

Table 4. Cemetery Samples: estimated mass loadings for leaf surfaces where at least 12 separate fields of view were analyzed. Particle size is expressed as the geometric mean. Mass loading results (median, (range) micrograms per square centimeter) are presented for all particles analyzed on each specimen, and for the estimated PM10 loading (features with optical diameters less than 6.32 μm).

				Mass Median Diameater (μm) at Percent Population			
Species	GM Size	Mass loading	PM10 loading	100%	99.9%	99.5%	99.0%
Apple	2.32 μm	4.5 (1-33)	1.1 (0.7-3.1)	17.7	11.5	6.2	6.0
Butternut	2.01 "	5.5 (1-18)	1.1 (0.5-2.9)	14.2	8.9	6.0	4.7
Cherry	1.97 "	4.5 (2-11)	1.1 (0.7-1.4)	10.1	9.0	6.3	5.2
Cottonwood	1.79 "	0.5 (0.1-7)	0.3 (0.1-0.6)	11.8	5.1	4.3	4.2
Lilac	1.62 "	4.4 (1-9)	1.4 (0.9-2.4)	8.6	6.7	4.2	3.5
Linden *	2.42 "	3.8 (1-6)	1.1 (0.5-3.1)	18.5	7.5	4.3	3.7
Oak	1.82 "	8.0 (5-37)	1.4 (0.7-2.9)	14.2	8.9	6.0	4.7
Pear	2.49 "	5.5 (1-12)	2.4 (1.0-4.2)	33.9	5.3	4.5	4.1
R Maple	1.83 "	3.0 (1-8)	1.1 (0.2-1.8)	7.8	6.1	4.9	4.2
S Maple	2.07 "	4.5 (3-14)	1.5 (1.1-2.2)	10.7	8.4	6.1	5.3
W Birch	2.03 "	6.0 (1-21)	1.6 (0.7-3.4)	12.4	11.5	8.0	7.0
D Fir	2.10 "	17.0 (8-24)	3.6 (2.4-8.1)	9.6	8.2	7.2	5.8
Ponderosa	2.23 "	50.0 (8-124)	5.5 (2.9-16)	16.5	12.1	11.2	8.1
Taxus	2.11 "	13.5 (2-68)	2.1 (0.4-8.8)	22.0	11.5	8.7	8.3

* sample collected October 1997

covering 12 contiguous fields of view each 0.36 mm^2 in area. For comparison, the douglas fir, ponderosa pine and *Taxus* samples were analyzed in a similar fashion with manual field selection. Results for these 14 species are presented in Table 4. Except for the linden and ponderosa pine specimens, these Cemetery samples were collected synoptically within a limited geographic range.

All these samples exhibited log normal size distributions, so the data summarized are reported as geometric means (and standard deviations). Not unexpectedly, mass loading estimates were also log normally distributed. This is illustrated in Figure 1 for the 11 deciduous species studied, where the cumulative probability plot (normal quantile) for the combined 132 SEM fields of view for the Cemetery samples is presented. As a group, the geometric mean mass loading was 3.7 ug/cm^2 with a geometric standard deviation of 1.4 -9.7 ug cm^{-2}. The conifer species were substantially higher in mass loading than the deciduous leaves. It is known that needles are more efficient impaction surfaces than are flat plates, but differences may also relate to the composition of the epicuticular wax of the conifers. The PM-10 loadings were about 1/4 of the total inorganic particle mass loadings and were generally in the range of 1-2 ug cm^{-2} for deciduous leaves, but were higher for the conifers.

The data in Table 4 and Figure 1 show a wide range of mass loading in the Cemetery samples despite limited spatial and temporal variability in the sampling. The area of leaf analyzed for each specimen (4.32 mm^2) and the number of particles characterized (685 for cottonwood, to 4450 for lilac) is insufficient to ascribe true species differences in the samples. In the present data set, the within species differences are on the same order as the between species differences; a few large particles can skew the results significantly. This is shown in the MMD results of Table 4. When the mass median diameter calculations are based on 100% of the particles analyzed, the Cemetery samples encompassed a four-fold range from 7.8 μm to 33.9 μm. If, however, the largest 0.1% of the particles is ignored for the computation, the results (99.9% column, Table 4) are much more consistent, ranging from 5.1 to 12.1 μm.

Few studies of a similar nature have been published. For deciduous species, the main comparison is with the results of Coe and Lindberg (1987). While they only examined two leaf specimens from chestnut oak for a total of 850 particles, the MMD of 10-11 μm reported agrees with the range of values we observed—8-33 μm (Table 5, 100% column). Coe and Lindberg found evidence of a bimodal size distribution for particles deposited on double-stick tape. However, particles on the leaf surfaces showed an approximately log normal distribution, in agreement with our observations, and with those of Butler (1988) for particles deposited on a polished graphite disc. The latter study showed a median particle diameter of 1.7 μm; we observed, as the volume equivalent diameter, the geometric mean to be in the range of 1.6-2.5 μm for the 14 different species of leaves and needles we examined. Coe and Lindberg (1987) reported 2.8 and 2.9 μm as the median particle size they measured on leaf samples.

The previous work by Fortmann and Johnson (1984a, 1984b) on *Taxus* needles collected adjacent to an industrial site showed a median particle size of 1.7 μm and a mass loading of 25.5 μg cm^{-2}. At a residential site, samples showed a median diameter of 0.8 μm and a mass loading of 12.6 μg cm^{-2}. In the present study, particles on *Taxus* collected at the edge of a parking lot on the SUNY ESF campus showed a larger geometric mean size (2.1 μm Table 4), but the mass loading of 13.5 μg cm^{-2} was similar to Fortmann's residential samples.

Uncertainty and Variability in Physical Measurements

The mass loading estimates are subject to a number of uncertainties. First, carbonaceous particles are generally not identified by the image analysis procedures, thus limiting the measurements to the inorganic fraction. Second, the prolate spheroid approximation overestimates the volume of flat or disc-like features and underestimates the volume of cylindrical or rectangular solids. Finally, application of an average specific gravity for the particles may have site-specific variability. However, within experimental uncertainty, the individual particle analysis mass loading estimates agree with the gravimetric determinations carried out on the ponderosa pine samples. The mean of 3 gravimetric measurements (50 needles each, approximately 11 mg of deposit) was 55 ± 5 μg cm^{-2}, whereas the IPA result was 50 ± 21 μg cm^{-2}. While further refinements and comparisons are necessary, the automated SEM IPA approach is clearly advantageous for direct estimation of particle mass accumulation on leaf surfaces.

We examined the issue of inter- and intra- leaf variability using one deciduous species, linden (*Tilia*

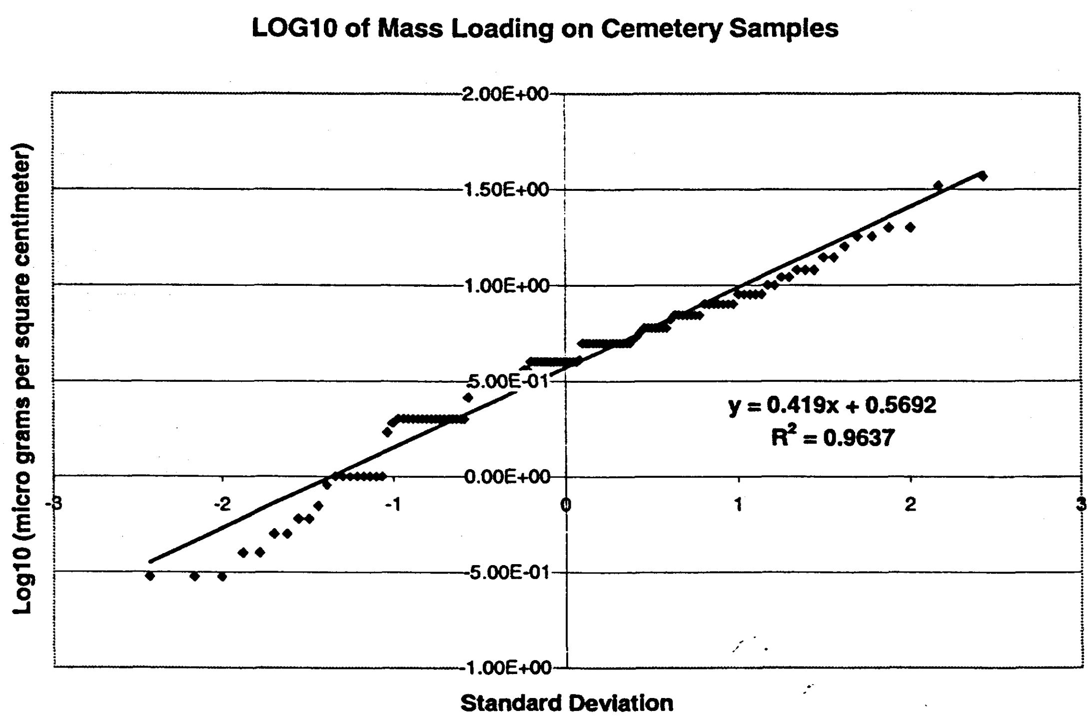


Figure 1. Normal quantile (cumulative probability) plot of particle mass loading (μg cm^{-1}) measured for 11 deciduous tree species growing in Oakwood Cemetery, Syracuse, New York, October 1996.

euchlora). While the population of particles on the linden leaf surface is log normally distributed, the spatial arrangement of deposition patterns is not random. Figure 2a shows the number of particles per field of view in the SEM, as a normal quantile plot for 72 contiguous fields covering an area of 7.2 x 3.6 mm^2. A contour plot of the particle number distribution for the same area is shown in Figure 2b. We analyzed several 72-field portions of linden leaves growing on the same branch, as shown in Table 5. Two leaves were analyzed in the 12 x 6 field pattern of Figure 2b (one of these in duplicate), and two leaves were analyzed as six separate specimens, each 4 x 3 fields of view, taken as a transect across the mid-section of the leaves. When compared at the 72-field level, mass loading variation between leaves was reproducible to about ± 6% at one standard deviation (leaves 1a, 1b, 2, 3, 4, in Table 5, mean mass loading = 2.96 ± 0.18 $\mu g\ cm^{-2}$). At the 12-field level, the between-leaf variation for the 10 leaves in Table 5 was about ± 23%; an average of 3.11 $\mu g\ cm^{-2}$ for leaf 1, while the other 9 entries in Table 5 gave a mean of 2.86 ± 0.65 $\mu g\ cm^{-2}$. The within-leaf variability of the linden samples is of the same order as that shown for the between-leaf analyses. The average coefficient of variation in mass loading for leaves 1-4 determined at the 12-field level was ± 23%, and if the data from the duplicate analyses (leaves 5-10) are included, the average coefficient of variation is ± 33% (median is ± 25%).

These results are useful for preliminary interpretations. Under the SEM conditions we used, a 12-field analysis covered approximately 5 mm^2 (4.32 mm^2 actual) with an uncertainty in mass loading estimate of ± 25%. When the area of analysis was increased to 25 mm^2 as in the72-field analysis, the mass loading uncertainty was on the order of ± 5%. The '5 square mm' analyses of different deciduous species shown in Table 4 are not sufficient to determine whether real mass loading differences exist between most of the species sampled. The extremes, oak and cottonwood, were statistically different at the 0.005 significance level. However, the other co-located and synoptically sampled deciduous species showed variability in the mass of particulate material deposits which was about the same as that shown in the sampling variability of a single species.

Table 5. Particle mass loading results for studies of variation within leaves and between leaves on linden (*Tilia x euchlora*) sampled October 1997. All specimens were taken from a single branch of 36 leaves. Uncertainties (± one standard deviation)

Leaf	Analysis areas	Mass Loading ($\mu g/cm^2$)
1a*	72 contiguous fields (12 x 6), mean of 6 each 4 x 3 blocks	3.02 (0.67)
1b	as above	3.20 (0.58)
2	as above	2.78 (0.44)
3**	72 fields from 6 samples taken as a transect across leaf, mean of 6 each 4 x 3 blocks	3.00 (0.85)
4	as above	2.79 (0.81)
5***	mean of 2 each 4 x 3 blocks	3.84 (2.13)
6	as above	3.94 (0.53)
7	as above	2.23 (0.30)
8	as above	2.30 (0.28)
9	as above	1.79 (1.22)
10	as above	2.83 (2.51)

* A 2 cm. x 2 cm. specimen taken mid-leaf half way between edge and mid-vein
** Six each 1 cm. x 1 cm. specimens taken mid-leaf on a transect
*** Two each 1 cm. x 1 cm. specimens taken mid leaf; one at 1 cm. from the leaf edge, and one at 1 cm. from the mid-vein

CONCLUSIONS

The IPA technique outlined here is suitable for direct characterization of the physico-chemical properties of particles deposited on many kinds of leaf surfaces. For optimum work, leaves need to have smooth flat surfaces and exhibit a low X-ray background. About 25% of the species we examined fulfill these criteria; apple, butternut, cherry, linden, oak and white birch are excellent candidates. The size distribution of particles we measured on leaf surfaces agrees what that of the limited previous investigations; median values for 14 species for this study fell into the range of 1.6 μm to 2.5 μm. With suitable specimen selection and preparation, automated SEM runs are feasible, providing analyses for thousands of particles in each sample. This capability can be used to quantify both intra- and inter-leaf variation, and ultimately the dynamics of particle interception and retention by different leaf surfaces.

For the species we studied, both the particle size and the mass of particle deposit per unit area of leaf were log normally distributed. Analytical reproducibility of the latter measure varied inversely with the area of leaf surface analyzed. For linden,

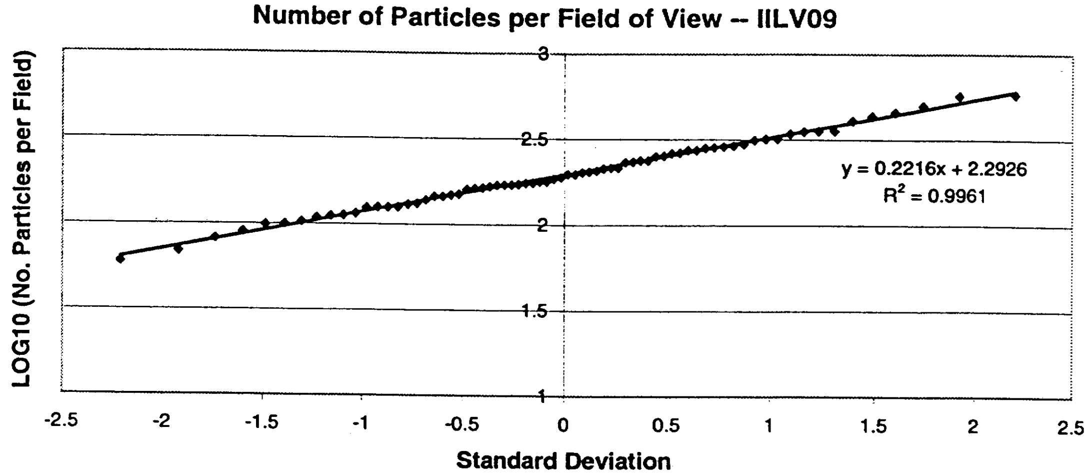
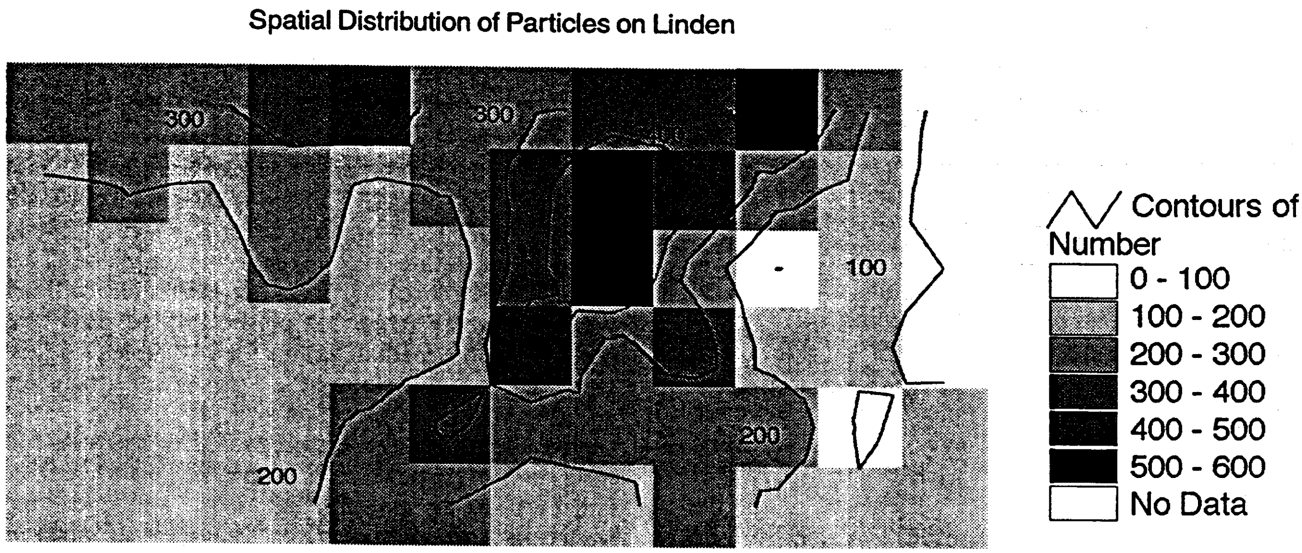


Figure 2a. Normal quantile (cumulative probability) plot of the number of particles per 0.60 x 0.60 mm. field of view on linden leaf ILV09.

the one species examined in some detail, analyses of 4-5 mm^2 of leaf area showed that for leaves growing on the same branch, variability within the leaves was about equal to variability between the leaves. It was on the order of ± 25%, but could be reduced to ± 5% if long analysis times (6-8 hr for 25 mm^2) were employed. Analyses of other species from the same location, and with the same sampling history, showed a similar variability in particle mass loading when 4-5 mm^2 of leaf were characterized. To determine the extent of real species differences in such cases, significantly larger leaf areas need to be analyzed.



Sample collected 10/11/97. Area analyzed was 72 fields of view, 7.2mm by 3.6 mm.
Contours represent the numbers of particles analyzed in each field of view (0.6 mm by 0.6 mm).

Figure 2b. Spatial distribution of particles on linden leaf ILV09 presented as population contours for a 12 x 6 (7.2 mm. X 3.6 mm.) field analysis area.

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