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Characterizing the Sources of Particulate Lead in House Dust by Automated Scanning Electron Microscopy

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■ Automated scanning electron microscopy procedures have been devised for apportioning the sources of lead in household dust. Source particles were sampled from auto exhausts, road dusts, garden soils, mineralized soils, paints, lead smelters, a waste incinerator, electrical materials, and lead oxide reference materials. A source signature library containing size and elemental data on more than 8300 individual lead-containing source particles was created. A divisive hierarchical cluster analysis was used to identify 101 groups of compositionally similar source "type" particles in the source library data. These groups formed the basis for an extended classification scheme. A simple descriptive apportionment procedure was defined to deal with the classification results generated by this scheme. The wide dispersion of lead in the house dust matrix necessitated the development of separation and preconcentration techniques involving density and size fractionation. Analysis results for house dusts suggest that paint, road dust, and garden soil may all be important lead sources. These contributions are a function of particle size, and the importance of the contributions is dependent on whether the apportionment is based on particle population or estimated particle volume.

Introduction

Elevated levels of lead in the urban environment have long been considered to have a potentially deleterious effect on human health. Within the urban community those most at risk are young children; in part this is because exposure to lead, even at relatively low levels, may have serious implications for the developing child (1–3). Also, by inadvertently ingesting dust lead through hand-to-mouth activity, children can be exposed to a source of lead not encountered by other groups. In the United Kingdom much of this hand-borne lead is likely to originate most immediately as settled indoor dust. This is a consequence of young children spending the majority of their time within the confines of the home. Concern over the presence of lead in house dust has prompted a number of studies aimed at quantifying the levels of lead within the home environment (4–12). However, such studies generally fail to address the question of source apportionment.

Identifying the contributions from the various sources of lead is a potentially much more difficult task. If dust lead loadings within a home are at an unacceptable level, then it is necessary to identify the source(s) before any remedial action can be taken.

In the ninth report of the Royal Commission on Environmental Pollution (13), it was recommended that research be devoted to assessing the contributions made by various sources to lead in dust. It is well recognized that in general the principal sources of house dust lead are paint lead, soil lead, auto exhaust lead (when lead is present as a fuel additive), and road dust lead. What is less obvious is which sources predominate at different scales of urbanization, in locations close to industrial activity, in areas with differences in local geology, and in homes of various ages. It is clear that in the case of house dust lead there is an interior–exterior source dichotomy. Of the interior sources, only leaded paint is usually of any significance. Under certain circumstances other sources within the home may be important (e.g., if related to some hobby or pastime of the occupant), but these are of limited extent. Lead-bearing paint particles become part of the household dust pool primarily from paint surfaces which are flaking or crumbling, or as a result of redecoration practices. Lead from exterior sources is integrated in a less direct manner. Airborne lead from vehicular and industrial emissions, plus lead which has been resuspended after deposition, is atmospherically transported into the home. Soil and road dust lead will be tracked in on footwear and by pets. Lead which is occupationally associated may be brought in on shoes and clothing (14–16).

Assessing the contributions from these sources has been attempted using stable isotope tracer methods (17, 18) and bulk chemical analysis techniques (10, 19). Source blurring due to the mixing of lead from different ore bodies is a potential problem for isotope ratio studies, while bulk analysis methods lack resolution because elemental composition differences for distinct sources are averaged together. An alternative approach to environmental lead tracing has been to employ scanning electron microscopy (SEM), in tandem with energy-dispersive X-ray analysis (EDX), to provide compositional and morphological data on individual lead-bearing particles (20, 21). These techniques are able to resolve sources whose emission products are compositionally similar at the bulk sample level but dissimilar at the individual particle level. Although the approach proceeds on a particle-by-particle basis, the

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time-efficient analysis of significant numbers of particles becomes possible by linking SEM and EDX through automated image analysis software (22). By using such a combination of techniques, it has proved possible to identify groups of lead-bearing particles, derived from different sources, in urban aerosol samples (23, 24). Until recently, however, the computer-assisted SEM/EDX approach has not been extended to the study of lead in indoor dusts. Over the course of a number of years, we have been developing methods for characterizing house dust lead by automated SEM/EDX. This work has proceeded in four main stages: (1) the generation of a library of source signatures based on the analysis of lead-bearing particles from a variety of sources, (2) the creation of a lead particle classification scheme, using the data in the source signature library, (3) the development of apportionment procedures to deal with the classification scheme results, and (4) the formulation of preparation and analysis protocols to deal routinely with lead-bearing particles in household dust. In this paper we describe each of these stages in detail. In addition, the potential for compositional variability that exists within house dust (a problem addressed in stage 4) is illustrated with results from various size fractions of house dust.

Experimental Section

Source Materials Collection. To develop a comprehensive library of source signatures, particles were collected from sources of environmental lead descriptive of the transport pathways into the home. Vehicular lead was obtained by sampling the exhaust stream of several stationary cars, which provided six samples vacuum-filtered directly onto 0.4- μm pore size Nuclepore polycarbonate membrane filters. This library of fresh exhaust particles was augmented by a set of pure lead halide crystals composed of PbClBr in the ratio 1:1:1. Leaded paint particles were obtained from 12 separate samples of interior paints and from 1 sample of yellow road paint. The interior paint samples were collected in the form of large flakes or chips from a number of households where older paint surfaces had become exposed as a result of either renovation or general decay. Samples of industrially emitted lead were collected from one secondary and two primary lead smelters. From these smelters, nine emission product samples were obtained either by scoop sampling or by use of a plastic dust pan and brush from various locations in and around the plants. These samples included furnace dust, distillation plant material, fuming furnace and lead softening process fumes, and sinter plant material. Samples of lead particles generated by refuse incineration were obtained from a municipal incinerator at Edmonton, London. Material was collected on three separate occasions within the stack by using a portable electrostatic precipitator (25). Urban road dusts and garden soil were also sampled as potential sources of lead. In the case of the former, the lead will generally be auto exhaust derived material, which may be fresh, aged, aggregated with other road dust constituents, or transformed by leaching. Road dust may also be contaminated by particulate lead from other adventitious sources. Garden soil lead will be either a natural constituent of the soil, the fallout from a variety of urban/industrial sources, or conceivably a product of indoor sources. In total, six road dust samples and five garden soil samples were collected from five and four different locations, respectively, throughout the London Borough of Richmond. Material was collected in the Richmond area as this was to be the setting for a subsequent detailed investigation into the sources of lead in urban homes (26). Road dust samples were collected as

gutter sweeping using a plastic dust pan and brush, while garden soils were obtained by scoop sampling material from the top 5 cm of exposed surfaces of the garden. Additional soil samples were collected (also by scooping and bagging) at three locations in the vicinity of the old lead mining villages of Derbyshire. These "mineralized" soils contain lead-bearing particles of different origin from those generally found in urban soils. Material representative of electrical usage (i.e., solder) was also sampled. This was collected both as a fume (directly onto 0.4- μm pore size membrane filters) and in the form of a fine powder. A final addition to the lead particle library were samples of lead metal and lead oxide powders (PbO , Pb_3O_4). Such material would be representative of particles which originated as metallic lead or particles which had been transformed in the environment to such an extent that they could only be identified as some form of common lead oxide.

House Dust Collection. As part of a study of the sources of lead in households in the London Borough of Richmond (26), dust was sampled from the household vacuum cleaner contents collected from 16 households in Richmond (27). This material was obtained in 1987 subsequent to the reduction of lead in U.K. petrol to a maximum of 0.15 g L^{-1} (28), leading to lower air lead levels in London by 1986 (29). As in previous studies (11, 19), the vacuum cleaner dust was initially passed through a 1-mm sieve to remove coarse carpet fibers (27) and this material was then subsampled for analysis.

Sample Preparation. Lead source samples acquired in the form of powders (including the process emission products) were each, initially, passed through a 64- μm nylon mesh and the 0-64- μm material was vacuum filtered onto 0.4- μm pore size membrane filters. Paint samples were treated in the same way after having been ground to a fine powder. The mineral soil samples were initially sieved down to 64 μm and were then deposited onto double-sided tape. The urban road dust and garden soils were also passed through a 64- μm sieve, but were then further preconcentrated by gravity settling in a heavy liquid consisting of a mixture of diiodomethane and xylene adjusted to a specific gravity of 1.9 g cm^{-3} . The resultant "sinks" [specific gravity (sg) $>1.9 \text{ g cm}^{-3}$] were washed in absolute alcohol and then mounted on 0.4- μm pore size membrane filters. Both double-sided tape and filter samples were subsequently attached to 25 \times 45 mm glass microscope slides, the latter with colloidal carbon paint, and were coated with a thin layer of carbon in a high-vacuum evaporator. Typically, several samples of each dust were prepared in order to obtain a suitable level of loading on the substrate. To avoid possible "contamination" of the X-ray signature of an individual particle by fluorescent X-rays from adjacent particles during the SEM analysis, only those samples where the particles were separated from each other by roughly two or more particle diameters were examined.

Household dust is an extremely heterogeneous mixture of mineral and organic components in which lead, when present, is usually widely dispersed. A practicable physical separation of the lead particles is a necessary prerequisite for time-efficient SEM analysis. Therefore, a simple sink-float separation was affected with a cutoff point of 1.9 g cm^{-3} . This was chosen to produce the greatest degree of separation between the organic constituents and the inorganic house dust particles which, generally, have an sg $>2.0 \text{ g cm}^{-3}$ (30). A size separation of the "sinks" was also affected to increase the efficiency of the SEM analysis. By confining the material to a limited size range an in-

dividual filter could be scanned at a fixed magnification. SEM analyses were generally conducted at either 1000 \times , 600 \times , or 200 \times , depending upon the size fraction under examination. The sample preparation proceeded as follows:

Two 0.5-g subsamples of <1 mm size dust were each added to 50 mL of diiodomethane and xylene adjusted to a specific gravity of 1.9 g cm⁻³. This admixture was ultrasonically agitated for 5 min and then centrifuged at 2000 rpm for 20 min. After centrifugation, the mat of floats collected at the surface was manually disaggregated with a glass rod and the ultrasonication and centrifugation stages were repeated.

The separated "floats" (sg <1.9 g cm⁻³) were decanted and vacuum-filtered onto two 47-mm-diameter 0.2- μ m pore size PTFE filter. Both filtrate and heavy liquid were retained. The sinks were washed repeatedly in absolute alcohol and then sieved through 180- and 64- μ m nylon meshes. Particles in the 0-64- μ m size range were filtered onto a set of several 25- and two 47-mm-diameter 0.4- μ m pore size membrane filters. Representative subfractions were obtained by sampling the particulate material while in a suspension (in absolute alcohol) created by mechanical and ultrasonic agitation. Filter loadings were varied intentionally, and the most lightly loaded 25-mm-diameter filters were used for SEM analysis. Particles in the 64-180 μ m and 180 μ m-1 mm size ranges were washed off the meshes with distilled H₂O, subsampled from a suspension, and vacuum filtered onto a set of 25-mm-diameter 0.4- μ m pore size cellulose nitrate filters. In order to retain the particles on these filters for SEM analysis, the most lightly loaded were mounted on glass microscope slides and each was exposed, briefly, to a stream of hot acetone vapor. This cleared and collapsed the filters, leaving the particles adhering to the filter residue. All filter weights prior to and after filtration were recorded to provide data on the quantities of material present in each fraction.

Lead Analysis. Quantities of house dust floats and sinks from each size fraction were analyzed for lead by inductively coupled plasma atomic emission spectroscopy (ICPAES). Filter samples plus procedural blanks were placed in test tubes, and an admixture of nitric and perchloric acids in a ratio of 4:1 was added. The tubes were then placed in a deep heating block until the contents were digested. Finally, the samples were taken to dryness over 24 h and then leached in 2 cm³ of 1 M HCl. The heavy liquid retained after each preparation was also analyzed for lead. Each sample was taken to dryness, and the residue was subject to the same digestion procedure as the dust samples.

SEM/EDX Analysis. Individual particle analysis was performed on a JEOL 733 Superprobe SEM interfaced with a Link Analytical AN10000 X-ray analysis system. Individual particle analysis was automated using the Link Analytical feature analysis program DIGISCAN. This system automatically collects and stores both compositional information (in the form of X-ray data) and size and shape measurements for each feature (particle) targeted in the SEM. The DIGISCAN software allows up to 25 regions of interest or windows in the X-ray spectrum to be monitored. If net count corrections are to be made, at least 5 of these must be used as background windows; therefore, a maximum of 20 element windows can be monitored for each feature. In this study windows for lithophilic elements, which are likely to be associated with lead, were selected. Certain environmentally less common elements were also chosen as they are known, under certain circumstances, to be intimately associated with lead (e.g., Pb and Br in

vehicular exhaust). Windows for the following elements were selected: Na, Mg, Al, Si, P, S, Cl, Cd, K, Ca, Ti, Ba, Cr, Ni, Fe, Cu, Zn, Pb, and Br.

Analyses were performed at an accelerating voltage of 25 kV so that windows in the higher energy regions of the spectrum could be utilized. This enabled the concentration of lead to be determined from the L α line, thus avoiding the problem of Pb M α line and S K α line overlap. The X-ray data were collected with a constant beam current of 4 nA and the acquisition time per feature set at 5 s. The analyses were also conducted in the backscattered electron (BE) mode so that high atomic number lead-bearing particles could be specifically targeted for examination. The setup procedure for this involved altering the BE signal to produce a field of view on the SEM CRT in which a lead particle would appear white against a black, less strongly backscattering, background. The signal strength was adjusted until any adjacent particles with a lower mean atomic number composition "disappeared" into the background, but not beyond a point where there was any obvious degradation of the two-dimensional projected image of the lead particle. Then this high backscatter threshold image was reproduced on the AN10000 monitor by matching the signal acceptance thresholds on the AN10000 to the range of BE signal strengths exhibited by the lead particle. This high-threshold approach was adopted because in many samples lead-bearing particles are only a minor constituent, and without some method of targeting these particles, it would potentially be necessary to analyze many hundreds or thousands of sample particles to acquire data on a few tens of lead particles. At the outset of each analysis, the BE image thresholds were set by the analyst following the examination of several lead particles. The X-ray information acquired from the selected high atomic number features was representative of the total area of BE binary image within the threshold limits. This was because, under computer control, X-ray data were continually collected as the electron beam rastered backward and forward across the whole of the threshold feature, providing an area-weighted average composition. The size information collected on each feature (which included projected area and maximum, minimum, and mean feret diameters) was also sensitive to the threshold conditions in that these measurements were confined to the high BE threshold image. During automated feature analysis fields of view were scanned at a 512 \times 512 point spacing. The separation of these search points, at which the electron beam halted to determine the presence of a particle, at 1000 \times , 600 \times , and 200 \times was respectively 0.19, 0.32, and 0.97 μ m. The raw information obtained during each analysis was stored and subsequently processed using a PC-based program called MIDAS. This software was used to convert the raw X-ray counts (through a series of peak overlap and background corrections) to percentage net X-ray intensities for the selected 19 elements and to exclude from the data sets non-lead-bearing high atomic number particles by selecting only those with net X-ray counts in excess of 0.1%. The data interpretation capabilities of MIDAS (31) were also used to derive a classification scheme from the results in the source signature library.

Results and Discussion

Source Material Analysis. SEM/EDX data were collected on over 8300 lead-bearing source particles. A variety of element associations were identified in the particles from each of the generic sources. In general, these were consistent with the results of previous individual particle analysis studies and with the known origins of such materials. In the auto exhaust particles, for example, lead

was found to be largely associated with Br and Cl and to some extent with Fe and S (23, 24, 32, 33). In the road dusts, the lead-bearing particles were found to contain significant quantities of Fe, Mg, Si, Al, and Ca (20). These types of element associations, which were observed in each set of generic source particles, were used to develop a sorting scheme for classifying lead-bearing house dust particles.

It is possible to apportion particulate material in an ambient sample by working exclusively within the particle data. This involves identifying groups of "like" particles on the basis of similarities in morphology and/or composition by cluster analysis. The assignment of the defined particle groups to specific sources is then made based on the analyst's knowledge of the emission products of the potential sources. Applying this methodology to lead particles in the atmosphere of Antwerp, Belgium, Van Borm et al. (24) were able to conclude that such particles were derived from either car exhausts, soil, refuse incineration, or non-ferrous metal industries. An alternative to this approach, which is less dependent upon the assessments of the analyst, involves matching ambient particle results to data obtained from the analysis of source materials.

The lead source particle database was reduced to a manageable form by dividing the data into groupings based on similarities in composition and, hence, origin. From such groupings it becomes possible to identify the compositional attributes required for an unknown particle to be ascribed to a particular source. Very broad generic source groupings would be based on the elemental concentration ranges for all particles of the same generic origin (e.g., all auto exhaust particles). However, as most generic sources produce a variety of particle types, the elemental ranges which categorize a single generic source group will, necessarily, be wide enough to accommodate the various constituent particle types. Particles of somewhat similar composition but of different origin can easily be assigned to the same category. If the accuracy of particle classification is to be maximized, it is necessary to create a large number of categories, each of which reflects the composition of a specific particle type. To identify these subgroups of compositionally similar lead-bearing particles, a cluster analysis was employed that utilizes the shape characteristics of the cumulative normal distribution plot for each variable that describes the data set. These normal quantile (NQ) plots (which are a standard graphical output option of the MIDAS program) are produced by assigning quantile scores to the ranked data values for each variable. The median value (50% point) in the data list is assigned a quantile score of 0.0 (equivalent to the mean), the 15.9 and 84.1% values in the list are assigned scores of -1.0 and +1.0, respectively (corresponding to ± 1 SD), and so on. For the data variables, certain types of deviation from a normal distribution, which appear as departures from a straight line on an NQ plot, can be used to divide up a data set into meaningful subpopulations (32, 34). The basic principles involved are illustrated by Figure 1. If the lead concentration (in terms of relative X-ray intensity) within the population of analyzed particles is normally distributed, a single straight line would result. The marked departure from linearity indicates that there are at least two populations within the data set. One of these consists of a set of particles for which the lead relative X-ray intensities are between -1 and +2% and which can be thought of as the "zero population". In this group, where some of the relative X-ray intensities for lead are negative because of background overcorrection by the X-ray count

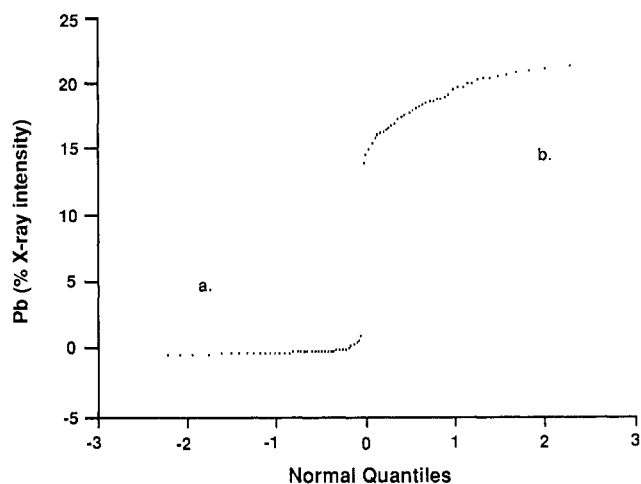


Figure 1. Quantile plot of the lead relative X-ray intensity's for a mixed population of particles consisting of a subpopulation of high-titanium paint particles without lead (a) and a subpopulation of lead-, bromine-, chlorine-, and iron-containing auto exhaust particles (b).

correction program, the range of lead X-ray intensities represents the uncertainty in detecting the presence of lead in a non-lead-containing set of particles. The other population for which the lead intensities are between 14 and 22%, in contrast, contains particles that have an appreciable lead content.

The creation of a lead particle classification scheme using this method of data clustering progressed in two phases. In the first, the data for each set of generic source particles was divided into groups using the NQ plot approach. The procedure is a divisive hierarchical one which proceeded in the following way. The results of the analyses of samples from one generic source were added together to form a single database. Then, the NQ plot for each of the variables in this database was examined and the variable with the most "significant" departure from normality (34) was chosen as the starting point for splitting the data set. The NQ plot for each variable in each subpopulation so generated was, in turn, examined to identify further possible "splits" in the data. This process was repeated until the variable data formed a single distribution, or the subpopulation contained less than 2% of the particles in the data set. At this stage, the variables used to identify groups within the data set may be referred to as "inclusive" variables. In the second phase, the objective was to minimize particle category description overlap by sifting the data for each particle in the entire source library through the categories defined by the inclusive variables. Those particles from each generic source which fell into categories defined by material from another generic source were then identified. For both these "misclassified" particles, and for those from which the category was derived, the ranges of the variables which were not originally specified as inclusive but which also characterize the particle data sets were defined. When any of the sets of "noninclusive" ranges showed no overlap, these variable ranges were used to specifically exclude particles from categories of a different source type. Such noninclusive variables, when added to the list of class descriptions, can be regarded as "exclusive" variables.

Partitioning the data in the lead source signature library by this technique was performed using the X-ray data for the 19 elements, the total X-ray count, and the gross X-ray count rate (GCR) as variables. The iterative procedure of category comparison and revision, using the known source materials, was guided by key associations between Pb and the other observation variables. Table I shows the

Table I. Key Primary and Secondary Observation Variable Associations for Lead-Bearing Particles from Each of the Generic Sources of Lead

sources	observation variables	
	primary	secondary
automotive	Br	Cl, GCR
paint	Ti, Ba	Ca, Zn, Fe, S, Cl
high temp ^a	Na	Cl, S, Zn, Cd, K
road	Fe, K, Mg	Al, Si, Ca
soil	P, Cl	Mg, Fe, Al, Si, Ca
electrical	K, Ca ^b	GCR
common and oxide ^c	GCR	

^a Includes refuse incinerator samples. ^b Results from characteristic Sn L X-ray overlap with K α X-ray energies for K and Ca giving distinct (apparent) K and Ca net X-ray relative intensities. ^c Includes Pb metal.

generalized variable associations from which the families of individual particle types were formulated. The presence of bromine in automotive emission particles was a major delimiter, though chlorine and a low GCR were also important in categorization, as was iron to a minor extent. Lead derived from paint was commonly seen in association with titanium or barium, though one or more of the secondary elements were also commonly present. High-temperature (smelter) emissions often contained particles with significant sodium (and usually chlorine), possibly from flux materials employed. Zinc and sulfur were sometimes present. Potassium and lead associations were found in incinerator-derived materials along with a low percentage of particles which also contained cadmium. Electrical sources (solder fume) were characterized by high GCR and distinctive ratio of K and Ca; the latter elements are artifactual since Sn X-rays overlap with the potassium and calcium K α X-ray energy regions. Road dusts and garden soil materials all showed strong covariance with the elements Si, Al, Ca, Mg, and Fe within family subgroups of particles. However, phosphorus and chlorine associations with lead were more common in soils, while Fe, Mg, and K were the major indicators for road dusts particles. Common lead oxides and lead metal showed distinctive differences in gross X-ray count rate. The limited number of particle shape parameters generated by the feature analysis software provided no useful discriminating information and were not used during the course of data splitting.

The key parameters listed in Table I were efficiently employed as both inclusive and exclusive variables in particle category development, though they were not unique discriminators. By way of illustration, the key element in automotive emissions, Br, was not always present in source particles and could not be consistently employed as an inclusive variable to exclude lead smelter particles (in which Cl was a major component) from the automotive exhaust categories. Examination of other variables showed that sodium was often present in the smelter materials but rarely found in the auto exhaust particles. By adding the ranges of the sodium "zero population" as a noninclusive variable to the appropriate automotive classes, it became possible to specifically exclude the sodium-bearing lead smelter particles from these categories. Bromine was absent from source materials other than automotive and thus its zero population values could be used to exclude most auto particles from those source family categories.

The cluster analysis resulted in the identification of 101 subgroups of particles. Generically, these divide into 11 auto exhaust groups, 11 road dust groups, 6 garden soil

groups, 2 mineral soil groups, 42 paint groups, 20 high-temperature process groups (smelters and incinerator), 2 electrical material groups, and 7 common and oxide groups. The common and oxide particle groups resulted from the analyses of lead metal and lead oxide particles and from the identification of certain compositionally similar particle types which derived from different source materials. In both cases, the particulate material can be considered to be common to various generic sources of lead (35). This commonality may be a function of the particle generation process; for example, lead oxide particles may be a product of many emission sources. Alternatively, common particulate material may be produced by a process of chemical alteration. Lead sulfate which results from the reaction of vehicle exhaust lead compounds with atmospheric ammonium sulfate may be indistinguishable from lead sulfate particles derived from other sources.

Each of the 101 sets of inclusive and exclusive variable ranges defines a particular category of particle and hence served as the basis for the classification scheme. For the purposes of classification, the variable ranges for each category of particles were organized into a linear sorting scheme. In this arrangement, classification was achieved by the sequential matching of the values of the observation variables of an unknown to the variable ranges in each category. This is a "first fit" classification method in that as the data are sifted through the scheme, once all the criteria specified for a match are met the sorting terminates. If the particle data did not match the criteria of any category, the particle was designated as miscellaneous lead-bearing. The particle categories in the sorting scheme employ ranges of values for 12–18 observation variables—hence, they are quite specific. Tests with known materials (e.g., pyromorphite mineral particles, additional lead chromate paint) not present in the original source library showed a majority of the particles as "miscellaneous". The MIDAS software can easily subset such features within a data set for further detailed treatment such as discriminant analysis (26).

Although a detailed division of the source data has been achieved with the NQ clustering procedure, it has not proved possible to effect a unique partitioning. In part, this is a reflection of the mixed origins of certain of the source materials. It is also a result of limitations in the analytical technique. With a fixed list of 19 elements, it is impossible to account for all the variability in the source material. Therefore, it is not surprising to find particles that are compositionally on the periphery of their own source group being accommodated within the bounds of a different source group. A measure of this overlap is provided by sorting the source material data through the classification scheme. The result of sorting the lead source signature data through the 101 category scheme is set out in Table II. In this compressed version of the classification, the percentage of particles falling into the individual categories of a generic source have been summed (i.e., the number of source particles classified by each of the 11 auto exhaust categories has been added to give a total auto exhaust value, etc.). From Table II it is clear that there exists a degree of classification overlap which, when particles of unknown origin are classified using the scheme, will be carried through.

Source Apportionment. In most individual particle source apportionment studies the problem of source signature overlap is dealt with by adopting a particle class balance receptor model approach (36). Previously, using an earlier and less comprehensive version of the lead particle classification scheme (37), it has been shown that

Table II. Classification Results for Lead-Bearing Particles from Various Generic Sources of Lead^a

classes	sources						
	auto	road	garden soil	mineral soil	paint	high temp	electrical
misc Pb ^b	5.2	4.4	6.8	0.0	7.7	1.4	1.7
auto	73.2	1.8	0.4	0.0	0.5	8.8	0.0
road	2.6	65.3	15.5	13.3	2.7	3.0	0.5
garden soil	0.7	10.6	61.9	11.4	0.3	0.2	0.7
mineral soil	0.0	0.0	0.0	57.2	0.0	0.0	0.0
paint	8.7	11.7	7.9	2.9	83.2	4.1	3.6
high temp	6.3	2.9	4.2	14.3	5.0	78.4	18.2
electrical	0.1	0.0	0.0	0.0	0.0	0.1	74.8
common and oxide	2.6	3.7	3.4	0.0	0.9	4.1	0.5

^a As a percentage of the total number of particles from each generic source. ^b Miscellaneous lead-bearing.

a simple linear least squares fitting model can be used to satisfactorily "unmix" house dust lead particle signatures into their fractional contributions. However, with the 101 category scheme described here, an alternative approach has been taken. From Table II it is clear that the greatest overlap is for those generic materials which cannot be considered as being derived from "pure" sources. It is, for example, quite likely that garden soils contain road dust, auto exhaust, and paint lead particles. The source signature overlap is, in some measure, related to the original choice of source materials, a selection which was made to reflect upon the routes of ingress into the home. Due to the nature of this overlap and because of the fine level of resolution achieved by the scheme, we hypothesize that the need for mathematical apportionment is obviated. Any results generated using the scheme are themselves the source apportionment. Uncertainties in the results associated with source sample overlap can be directly quantified from information in the source signature matrix.

Details of this simple descriptive apportionment approach have been described elsewhere (35). The essential features of the method may, however, be summarized as follows. The approach utilizes the results provided by the scheme and aims to estimate the overlap uncertainties on a category-by-category basis. The percentage of ambient particles falling in a specific category (e.g., one of the 42 paint categories), which are potentially derived from a different source (e.g., road dust "misclassified" because of source signature overlap), is estimated from numbers of particles that fall into the categories of the different source (the road dust categories) and the degree of overlap in the source signature matrix (road dust source particles falling into the paint category). The overlap estimate for the j th category in the scheme (O_j), which is a member of the set of categories derived from material from generic source L , is obtained from the expression

$$O_j = \frac{\sum_{i=1}^K f_w}{\sum_{i=1}^K (f_i/f_k) \times 100} (f_j/f_k) \times 100 \quad (1)$$

where f_i is the number of source particles from generic source K in the i th category of the scheme, f_k is the total number of particles from source K , f_w is the number of ambient particles in the i th category, and f_j is the number of source particles from generic source K in the j th category. The total number of potentially overlapping particles from source K in the categories of source L (O_{KL}) is obtained from the equation

$$O_{KL} = \sum_{j=1}^L O_j \quad (2)$$

This expression readily provides a descriptive estimate of the potential error associated with a source apportionment.

House Dust Analysis. Density separating the house dusts resulted in a major division of the sample mass. Approximately half of each sample was "floated off" during the separation (Figure 2b). This is consistent with estimates for organic matter content of house dust of 40–50% as determined by weight loss on ignition (10). The "floats" largely consisted of organic materials including fibers, food residues, insect parts, and biological remnants (Figure 3a). The heavy fraction of the dust consisted mostly of glass fragments, mineral grains, paint particles, and metal shards (Figure 3b). A proportion of each house dust was lost during the course of preparation. In part, because the separated fractions were, on average, collected on 19 individual filters, this can be attributed to handling losses. It is also likely that some fraction of the house dust was dissolved by the heavy liquid during processing.

The density separation procedure successfully concentrated the greater portion of the house dust lead in the heavy fraction. Bulk lead determinations by ICPAES on samples from the individual fractions (weighted by the mass in each fraction) indicate that 76.6% (median value) of the total lead was isolated in the "sinks" (Figure 2a). The remaining lead is likely to be bound with the organic matter in the "floats" or is associated with particulate material not split off during the density separation (26). Analysis of the retained heavy liquid showed that no more than 0.3% of the total lead in any house dust was taken up by the heavy liquid during sample processing.

Particulate lead in the sinks was found to be widely distributed amongst the house dust particles in each of the size fractions. An example of the type of filter loading for material in the 64–180- μ m fraction is set out in Figures 4a. The particulate lead concentration in the individual samples was highly variable. Figure 4b, which is the high-threshold BE image of the field in Figure 4a, is illustrative of a sample with a large quantity of high atomic number features. The variation in particle size in this sample may be the result of inefficient sieving or the result of particle breakup during the final stage of ultrasonic agitation. In most samples the lead-bearing particles were present in low concentrations, and for the purpose of analysis, it was generally necessary to scan large portions of one or more filters. It was found that the most efficient method of analysis involved dividing the filter into a grid of several hundred fields of view which could be scanned automatically using stepper motors to control the movements of the SEM stage.

Size fractionation of the house dusts prior to analysis allows the particle size dependence of the individual source contributions to be investigated. Targeting lead-bearing

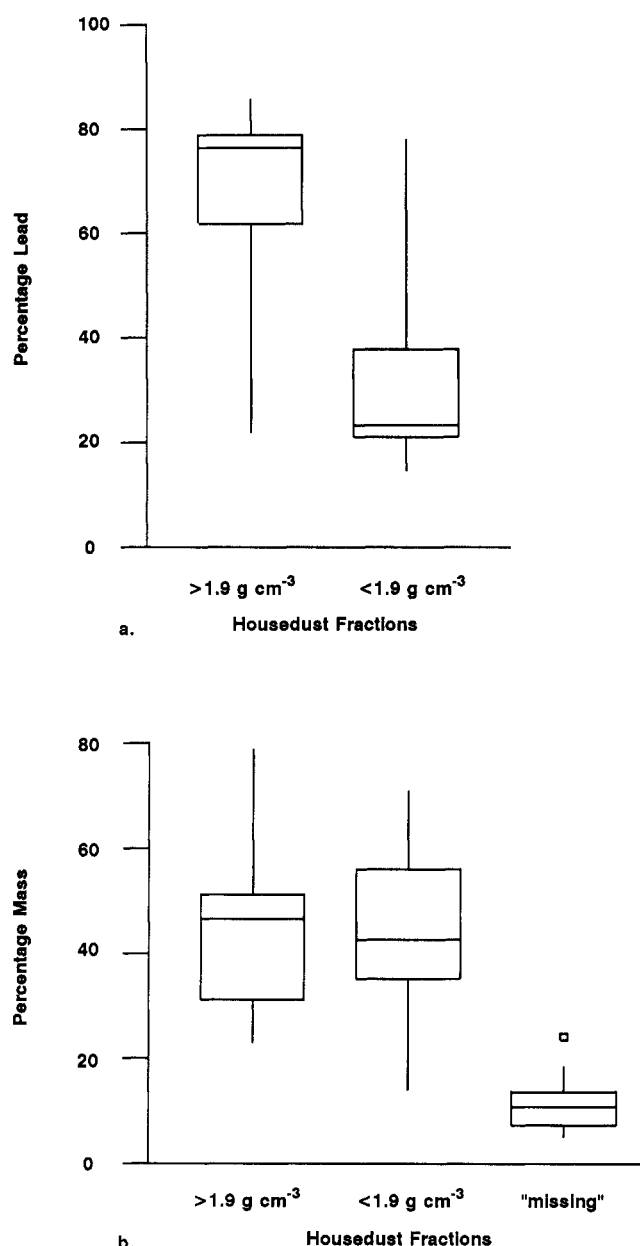


Figure 2. Box plots of the percentage lead in the house dust fractions of >1.9 and $<1.9 \text{ g cm}^{-3}$ (a) and the percentage mass in the same fraction and that in the fraction lost on processing (b). (The central bar defines the median, the box length the interquartile range, the whiskers the range, and points any value greater than 1.5 times the interquartile range.)

particles by using the high BE threshold image means that large particles which contain lead inclusions are broken down into a number of features which, in the absence of any size fractionation, would be difficult to distinguish from individual lead particles of smaller size. This is illustrated by some preliminary results from two of the Richmond house dusts (Figure 5). The percentage of particles derived from each generic source in these houses was determined by the numbers of ambient house dust particles falling into each category of the 101 category classification scheme. The classification uncertainties, which are presented as the percentages of particles potentially derived from other sources (shaded area of the stacked histogram), were determined using the apportionment approach outlined previously. From the results presented in Figure 5a, it is apparent that on a particle number basis in each of the size fractions in house 94 the dominant source of lead particles in paint. In contrast,

in the dust from house 81 there is considerably greater compositional variability (Figure 5b). In this case, while lead-bearing paint particles are the major contributors in the $64 \text{ }\mu\text{m}$ – 1 mm size range, in the 0 – $64\text{-}\mu\text{m}$ range, the dominant sources of lead are road dust and garden soil. This relationship would not necessarily have been apparent if preanalysis size separation had not been undertaken.

In terms of particle size, the diameter data for the lead-rich particles in the 0 – $64\text{-}\mu\text{m}$ fraction of both house dusts were found to be log-normally distributed. The mean particle diameter in this fraction, based on the average of 60 feret diameters measured for each particle, ranged from 0.3 to $10.7 \text{ }\mu\text{m}$ (geometric mean $0.9 \text{ }\mu\text{m}$) and from 0.6 to $2.9 \text{ }\mu\text{m}$ (geometric mean $1.4 \text{ }\mu\text{m}$) for houses 81 and 94, respectively. However, as these measurements were obtained using a high backscatter electron threshold image, it is possible that they are not representative of actual particle size. As these data were collected using a single high threshold it is not known, in individual cases, whether the lead-rich features were constituents of physically larger particles. Certainly, in the coarser size ranges, where the lead-bearing particles are, for the most part, likely to be present as inclusions in larger paint fragments, this will be the case.

The results presented in Figure 5 are based on the numbers of lead particles classified by the scheme. A perhaps more environmentally significant apportionment would be based on particle volume or mass. As the analyses performed here are based on high backscatter threshold features, it is difficult to arrive at data for particle mass. However, estimates for the volume of each lead feature can readily be obtained by using the stored size parameters and assuming each to be a prolate ellipsoid rotated about its long axis. Volume apportionment results for both houses are presented in Figure 6. The volume percentages have been arrived at by summing the volumes of all features assigned to the constituent categories of each generic source type. The uncertainty calculations associated with these apportionments are based on the numbers of overlapping source particles in each category. In the case of house 94 (Figure 6a), because the predominant contributor on a number basis in all size ranges is paint, the contribution pattern on a volume basis changes little. In the case of house 81 (Figure 6b), on a volume basis it is clear that the dominating contributor to the 0 – $64\text{-}\mu\text{m}$ size range is paint. It appears that in this size range, although road dust and garden soil lead particles exceed the paint lead particles in number, the few paint particles which are present are much larger than the particles from other sources.

The contributions from automotive exhaust to both house dusts is apparently low. While this may be the case, if the signatures of the exhaust lead particles have been altered in transport, the exhaust material may not register in the auto exhaust source categories. A proportion, therefore, may classify as road dust, which, to a large extent, represents modified exhaust lead. If the auto particles have been inseparably aggregated with other particulate material, the resultant mixed signature, if unlike any other in the source signature library, may identify these particles as miscellaneous lead-bearing. Previously, however, it had been found that by adopting a high threshold approach it is possible to identify exhaust lead particles in unseparated house dusts that were not initially detected using normal thresholds, presumably because of aggregation (38). In the situation where the aggregate particle signature matches some different source category, this is a source of uncertainty that will require the mea-

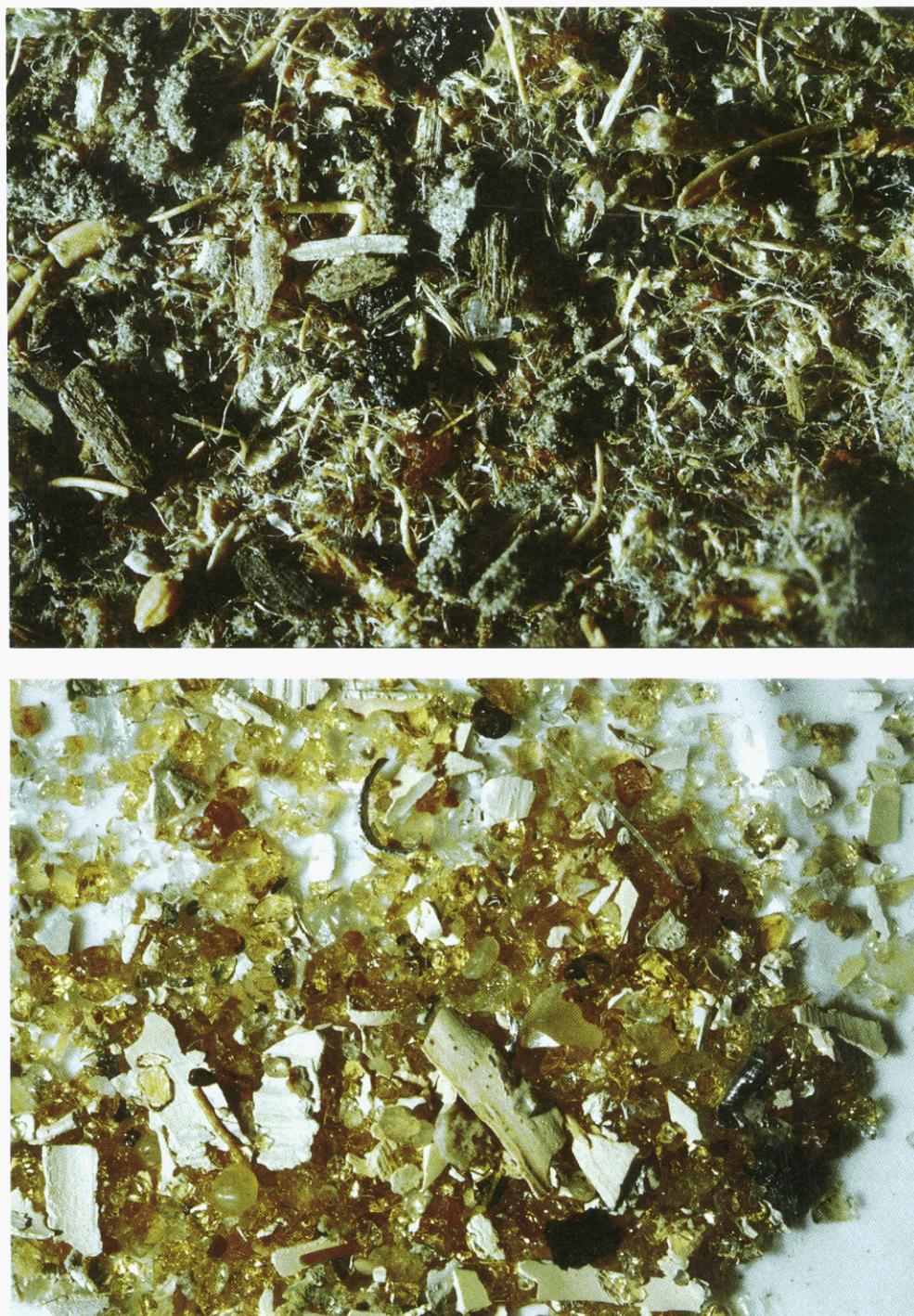


Figure 3. Photomicrographs of house dust "floats" (a, top) from Richmond house 81 (field width approximately 2.5 cm) and "sinks" (b, bottom) in the size range 180–1000 μm from Richmond house 94 (field width approximately 1.7 cm).

surement of more analytical components to resolve.

Summary

The automated SEM/EDX technique provides a powerful tool for apportioning the sources of lead in environmental samples. In comparison to bulk analytical techniques, the approach achieves a substantially greater degree of source resolution through its ability to partition data into a larger number of components. The methodology described here generates essentially semiquantitative results. The elemental concentrations which have been derived for each individual particle are nonquantitative.

Rather than rigorously defining particle composition, the aim has been to separate "like" from "unlike" particles. With the development of a classification scheme containing 101 categories based effectively on only 19 elements, clearly, this approach has proved successful. The level of resolution which has been attained is, in part, due to the choice of clustering technique. In contrast to unsupervised methods of clustering, the "manual" nonnormal clustering procedure adopted here permits analyst intervention at all levels. Consequently, on occasion, the analyst's experience can be used to provide environmentally meaningful partitions in the data. We have suggested that the ex-

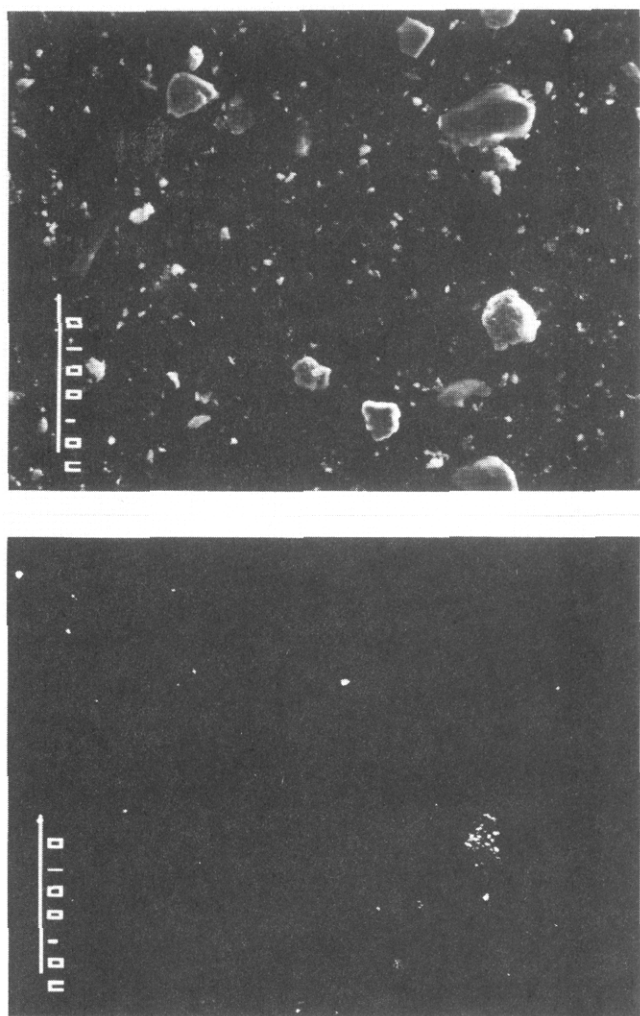
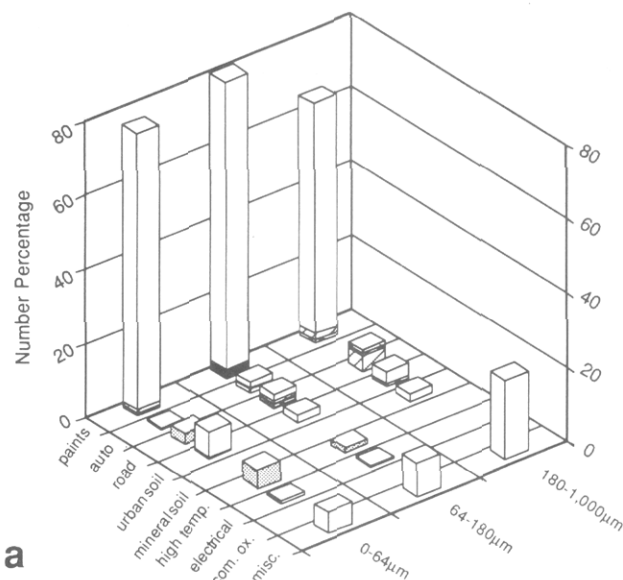


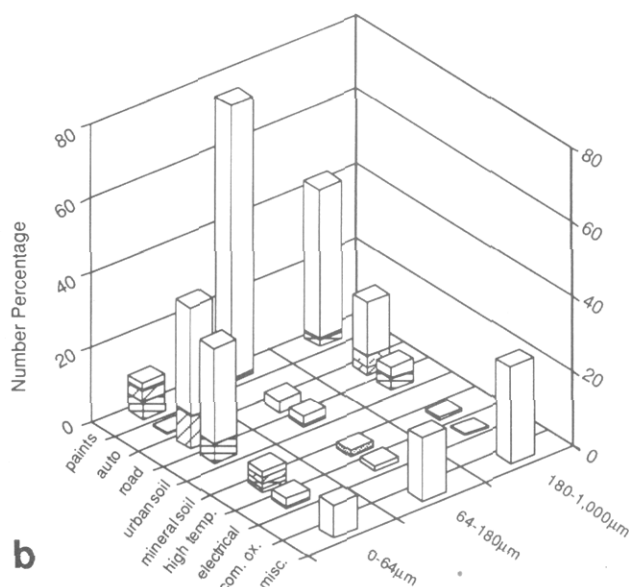
Figure 4. Secondary electron image (a, top) and backscattered electron image (b, bottom) of house dust in the 64–180- μm size range from Richmond house 94 (bar marker 100 μm).

tended classification scheme derived by this clustering method contains enough categories for ambient particle assignments to be regarded as the source apportionment. The overlap uncertainty estimates which accompany these results are arrived at on a category-by-category basis. As some categories are more efficient than others, this approach has the advantage of providing such estimates for only those categories to which ambient particles are assigned.

Household dust is an extremely complex medium with a degree of heterogeneity that makes it difficult to investigate the lead component. The apportionment results presented in Figures 5 and 6 must be regarded as being restricted to "SEM-accountable lead". This is the lead identified in the high average atomic number features. Lead which is present below the detection limit of the instrumentation will not be part of the source apportionment. This trace lead will include that lead fraction which is organically bound and lead which is present in small quantities in the crustally derived particles. Also, because the accountable lead is, generally, widely distributed throughout the dust matrix, hence necessitating the use of a high BE threshold, it is difficult to determine the full composition of many lead-bearing particles. Furthermore, in the case of certain large particles where the lead inclusions are not directly observable (e.g., on the surface in contact with the substrate), the quantity of lead present will be underestimated. These factors make it difficult to relate the quantity of lead determined by SEM/EDX



a



b

Figure 5. Number percentages of lead-bearing particles from the $>1.9 \text{ g cm}^{-3}$ fractions of Richmond houses 94 (a) and 81 (b) directly assigned to each generic source category. Shaded areas represented the percentages potentially originating as paint (□), auto exhaust (■), road dust (▨), urban garden soil (▩), and all sources in excess of the individual total (⊞) (other sources $<1\%$).

analysis to the quantity determined by bulk analysis. Although the SEM/EDX technique is unable to determine the total amounts of lead from contributing sources, its identification capabilities provide the most detailed information on the relative contributions from each source. These capabilities will continue to be enhanced with subsequent improvements in resolution. Such improvements will be brought about by measuring more analytical components. These will include (1) additional element windows in the X-ray spectrum, (2) morphological parameters which quantify particle shape, and (3) measures of the BE signal strength. Additional improvements will be brought about by advances in data acquisition. Through the implementation of multiple threshold procedures, the gathering of compositional and size data for a whole particle of which several lead particles may be part will produce additional discriminating information and will

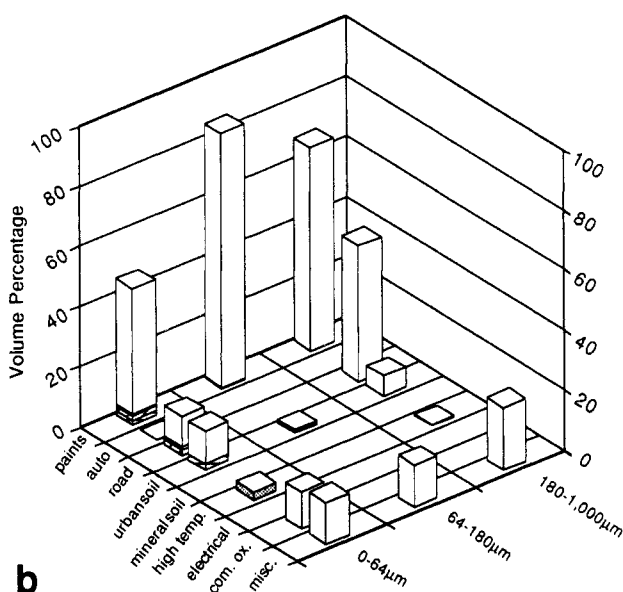
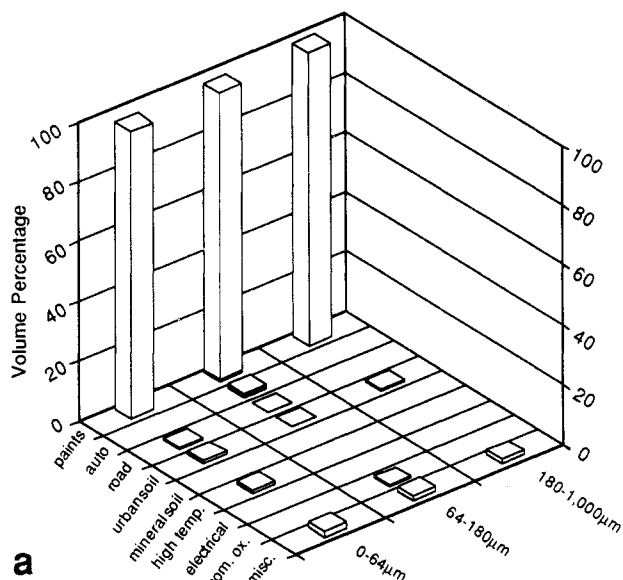


Figure 6. Volume percentages of lead-bearing particles from the $>1.9 \text{ g cm}^{-3}$ fractions of Richmond houses 94 (a) and 81 (b) directly assigned to each generic source category. Shaded areas represent the percentages potentially originating as paint (■), auto exhaust (■), road dust (■), urban garden soil (■), and all sources in excess of the individual total (■) (other sources $<1\%$).

make it possible to determine the actual number of dust particles which carry the lead.

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Amine-Algae Interactions: Cation Exchange and Possible Hydrogen Bonding

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■ The sorption of amines on algae in acid media was found to be similar to that of metals, which occurs via an ion-exchange process. Protonated ethylenediamine and ethyl glycinate were found by ^{14}C labeling to displace Ca, Mg in equivalent amounts on sorption by *Vaucheria* sp. In turn, they were displaced by Sr^{2+} , thus demonstrating the process to be one of cation exchange associated with anionic cell wall components. By use of Ca, Mg release as the measure of sorption, seven monoamines gave Langmuir adsorption equilibrium constants, a measure of bonding strengths, of $77 \pm 10 \text{ N}^{-1}$ and maxima of $409 \pm 46 \mu\text{equiv g}^{-1}$, indicating little structure effect. On the other hand, equilibrium constants for the C_2 , C_4 and C_6 diamines were 317, 1361, and 1564 N^{-1} , respectively. The low values for three amino acids ($55 \pm 7 \text{ N}^{-1}$) indicate a repulsive effect of carboxylate anions. Sorption of neutral ethylenediamine on algae occurs at pH 10, possibly due to hydrogen bonding to anions and hydroxyl groups.

Introduction

Various aspects of amine-algae chemistry are of environmental concern, since amines both promote and inhibit the growth process. It is well-known that added diamines interact with nucleic acid and are important as a means of controlling the growth process in animals, plants, and microorganisms (1), and in *Chlorella* the concentration levels of diamines parallel the extent of DNA replication (2). On the other hand, C_1 - C_6 aliphatic amines greatly inhibited the photosynthesis and nitrogen fixation of *Chlorella ellipsoidea* (3), and long-chain (C_{12} - C_{15}) amines are very strong inhibitors of the growth of microalgae (4). Amines can be formed from metabolism of proteins and decarboxylation of amino acids (5-7). Important environmental consequences arise from the fact that cattle feed lots generate considerable amounts of the short-chain amines, which accumulate in surface water to concentration levels toxic to *Chlorella* (3). Similarly, high concentrations of the long-chain amines arise from metallurgy processes used for recovery of silver (4).

Our previous work with algae has been directed to understanding the nature of the interaction of metals with algae (8, 9). From the pH behavior of metal sorption it was concluded that metals exchange at carboxylate or sulfate sites (10), probably of anionic wall polysaccharides (11-14). Cu sorption on *Vaucheria* at pH 7, carried out in the presence of ethanolamine (15) or ethylenediamine (en) (16) to prevent hydroxide precipitation, involved

cation displacement of $\text{Cu}(\text{NH}_3)_4^{2+}$ with Ca, Mg of the cell wall (17). At higher pH's the amine was itself strongly sorbed (16, 17).

We now report results on sorption of seven monoamines, three diamines, and three amino acids on *Vaucheria* in order to determine structural effects on this process. Strength and extent of sorption were measured by a new technique whose validity was tested in the present study by use of radiolabeled en and ethyl glycinate (etgly). This technique, measuring the extent of sorption by the amount of displaced Ca, Mg, was also used in a study of heavy metal sorption by algae at pH's where the insoluble metal hydroxides were present (10, 18).

Methods and Materials

^{14}C -Labeled ethylenediamine (en) was obtained from Amersham, and ethyl glycinate (etgly) from DuPont. The other amines were supplied by Aldrich. A Perkin-Elmer Model 2380 atomic absorption (AA) instrument was used for metal analysis, and a Searle Isocap/300 for ^{14}C counting.

Alga Preparation. The alga *Vaucheria* sp. was obtained from a local limestone spring. After thorough washing, the moist mass was stored at 0°C and used within 3-4 weeks. Before use a sample was cut to 1-3 mm for good mixing and was washed thoroughly with water. A suspension was stabilized at pH 5 with acid and filtered, and the sample was washed again to remove metals displaced by the added acid. Fresh water was added and the new suspension brought to pH 5 for use. All filtrations consisted of pouring a suspension onto a 40-60-mesh stainless steel wire screen.

Sorption of Amines. The sorptions of en and etgly were obtained by using the ^{14}C tracer technique. For other amines sorption by the protonated form was obtained from the amount of Ca, Mg released (see Ca, Mg procedure below). In both methods data were taken at ~ 5 min after mixing, when uptake appeared essentially complete.

For ^{14}C analysis, solutions (10 mL) were prepared at en (or etgly) concentrations of 1, 2, 3, 5, 7, 9, and 11 mM at the desired pH (5, 8.3, 11). To each was added an amount of ^{14}C -labeled stock to give 300-600 counts/min for a 200- μL aliquot. This gave the starting counts C_0 . The algal suspension (0.25 g in 200 mL) was brought to the desired pH and held there by addition of acid (or base) until stable. Portions (20 mL) were filtered, and the sample algal mass was paper-dried. These samples (~ 0.03 g) were put in the