Chemical Mass Balance Source Apportionment of Lead in House Dust

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Chemical mass balance was used to apportion the major proximate contributors of lead mass to house dust (HD$_{Pb}$) obtained from urban Jersey City, NJ, homes of children at risk for lead exposure. Coarse (up to ∼60 μm) and PM$_{10}$ (<10 μm) particle size fractions of vacuum dust samples from 64 residences with lead-based paints were analyzed for Pb and 16 other elements. Source profiles were developed to represent proximate source media contributors to HD$_{Pb}$ pre-1960 interior lead-based paints, indoor air, and a crustal source profile that accounted for the contribution of yard soils and street dusts. On average for both size fractions the exterior proximate sources, i.e., crustal materials and deposited airborne particulates, were responsible for approximately two-thirds of the HD$_{Pb}$ mass; the interior lead-based paint sources contributed the remaining third. Results indicate considerable variability in Pb source contributors between homes, but little difference in the source contributors to the two overlapping size fractions within homes. Effective reduction of HD$_{Pb}$ levels will require control of both exterior and interior sources.

Introduction

Elevated house dust Pb (HD$_{Pb}$) levels in urban environments are strongly associated with lead poisoning in preschool children (*1*). Primary sources of HD$_{Pb}$ particles include industrial emissions, deposited emissions from leaded automobile fuels, and chipping, cracking, and chalking of interior and exterior lead-based paints (*2−5*). Indirect pathways link primary sources via intervening media, such as exterior dusts and outdoor air, to house dust (*2*). The primary proximate sources of HD$_{Pb}$, i.e., the penultimate environmental media before house dust, are deteriorating interior lead-based paints, indoor air, and tracking-in of yard soils and street dusts on clothes, shoes, and pets.

Regardless of the ultimate source, the primary route of exposure in young children is ingestion of lead-bearing dust via hand-to-mouth behaviors (*1*). Little is known about the particle size distribution of dust ingested by preschool children, but the size distribution of dust adhering to the hand is usually assumed to be a surrogate for the ingested fraction. Dust adhering to the hand has been estimated to consist of particles with a maximum diameter of approximately 200 μm, with the vast majority of particle mass in the <10 μm size fraction (*6−7*). Apportioning the major proximate contributors to Pb mass in the particle size fraction adhering to the hand can help clarify the relationship between sources and Pb exposure by the hand-to-mouth pathway. Such research provides information needed to develop strategies for exposure reduction and effective risk management.

Researchers have used enrichment factors, chemical mass balance, relative lead concentration, isotope ratio, and scanning electron microscopy methodologies to estimate Pb source contributions to various particle size fractions of dust (*3, 4, 8, 9*). These studies have found that lead-based paints, soils, and road dusts contributed significantly to urban HD$_{Pb}$. Few studies have explicitly addressed the mass balance relationship between specific sources and HD$_{Pb}$ (*3*). This study examines the mass balance relationship between HD$_{Pb}$ and its proximate source media: indoor air, interior lead-based paints, and crustal sources, i.e., soils and street dusts.

Dust samples used for source apportionment came from households with interior lead-based paints screened for participation in the Children's Lead Exposure Assessment and Reduction Study (CLEARS). CLEARS was a randomized trial designed to test the efficacy of careful household cleaning and maternal education in reducing blood lead levels in preschool children (*10*). Families with occupational exposure to Pb were excluded from the study to control for the effect of the intervention. Representative dust samples were resuspended in a laboratory suspension chamber to obtain two size fractions: total suspended particulate (hereafter coarse) and <10 μm (PM$_{10}$). The coarse fraction comprises all particles (including PM$_{10}$) with aerodynamic diameters less than approximately 30−60 μm (*11*).

Chemical Mass Balance Receptor Model. The primary assumption behind a mass balance model is that the mass of HD$_{Pb}$ or any other chemical component of house dust, is the sum of the mass contributions from all source pathways. By characterizing the chemical composition of each source, a multispecies mass balance can be performed. To perform a chemical mass balance (CMB) of HD$_{Pb}$ a source apportionment modeling technique used most commonly in air pollution studies, receptor modeling, was adopted (*12, 13*). EPA-sanctioned software has been developed (*14*), and CMB's strengths and weaknesses have been extensively examined (*15−17*). The six basic assumptions of the CMB model are summarized elsewhere (*13, 15*). While it may not be possible to meet all assumptions in many cases, it has been demonstrated that the CMB model can tolerate reasonable deviations from these assumptions. Such deviations may result in increased uncertainties calculated by the model for its source contribution estimates (*14, 15*). In this study, CMB was applied to estimate the fractional Pb contribution to HD$_{Pb}$ from the proximate sources interior lead-based paint (LBP$_{Pb}$), indoor air (AIR$_{Pb}$), and crustal sources (CR$_{Pb}$ including soils and street dusts).

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A CMB analysis consists of a least-squares solution to a set of linear equations:

$$HD_i = F_{i1}S_1 + F_{i2}S_1 + ..F_{ij}S_j. + F_{iJ}S_J$$
$$\text{for } i = 1, ..., I, j = 1, ..., J \quad (1)$$

where HD_i is the concentration of element i in house dust (e.g., HD_{Pb}), F_{ij} is the fraction of element i in the dust sample from source j, and S_j is the fraction of the mass contributed to the dust sample from source j (e.g., air, crustal, etc.), I is the number of chemical elements, and J is the number of source types (14). Input values of mass concentration and measurement uncertainty for the HD_i and S_{ij} matrices are required to perform a CMB analysis.

CMB's simultaneous equations are solved by an effective variance least-squares estimate calculated from the measured uncertainties in the source and receptor media concentrations (14, 18, 19). The effective variance weighting method gives greater weight in the least-squares solution to elements with higher measurement precision in both the source and receptor media.

Materials and Methods

House dust and proximate source media samples were collected in Jersey City, NJ, using protocols developed for CLEARS and analyzed for multiple elements using X-ray fluorescence (XRF) at two laboratories (20). Both XRF systems were capable of measuring elements from Al to Pb with detection limits ranging from percent levels to approximately 10 ppm, depending on the element, and were designed for analyzing aerosols collected on thin filters. This constraint required that the house dust and source media be resuspended and deposited onto thin membrane filters for analysis. Analysis of house dust was performed at the Desert Research Institute Laboratories in Reno, NV. Analyses of the proximate source media were performed at EPA's National Exposure Research Laboratory (NERL) in Research Triangle Park, NC.

House Dust Sample Collection and Analysis. Dust samples used in this study were selected from the set of CLEARS samples collected at the study's first home visit (i.e., baseline), before instituting the home cleaning intervention. Dust samples were collected from wall to wall carpets and area rugs ≥ 48 ft^2 in 64 homes between June 1992 and November 1994 using a vacuum cleaner developed for CLEARS and calibrated for the effects of temperature, relative humidity, carpet type, and vacuum inlet face velocity on collection efficiency (21). All samples were collected in a filter bag placed in the vacuum cleaner nozzle, which had a minimum collection efficiency of 95% for 0.1 μm of particles. Samples were collected from children's primary activity areas, which varied from home to home, and included living rooms, bedrooms, and kitchen floor carpets. More than 80% of the residences sampled were small apartment buildings with 3–20 units; the remaining residences were either high rise apartments buildings (~10%) or single family detached or town homes (~10%). All residues were built prior to 1960, with the majority built before 1940.

Particle Resuspension. Before resuspension, house dust samples were sieved to <500 μm to remove carpet fibers, insect bodies, and other large particles. Sieved dust samples were then resuspended onto 47 mm Teflon filters (Gelman Teflo, R2PL047, Ann Arbor, MI) using a forced air resuspension chamber system (11). A minimum of 1–1.5 g of sieved dust was needed to achieve target loading levels of 1–3 mg of dust per 47 mm filter necessary for quantitative XRF analysis (22). Coarse fraction samples were obtained by collecting all resuspendable particles on filter media: particles from <1 μm up to approximately 60 μm aerodynamic diameter. The coarse fraction of six house dust samples were resuspended onto 47 mm quartz-fiber filters (Pallflex 2500 QAT-UP) to facilitate carbon analysis (23). Size selective impactors were used to obtain the PM$_{10}$ (≤ 10 μm) fraction. For most soils and dusts, approximately 50% of the mass in the coarse fraction consists of particles ≤ 10 μm (11). The PM$_{10}$ fraction was examined to determine if source contributions for particles >10 μm differ from those in the ≤ 10 μm size fraction, because particles ≤ 10 μm adhere more strongly to the skin than larger particles (6) and because particles ≤ 10 μm are more easily absorbed in the gastrointestinal tract (24). As part of the quality assurance program, National Institute of Science and Technology Standard Reference Materials (NIST SRM) 1579 (powdered lead-based paint), 2709 (low trace metal concentration soil), and 2711 (high trace metal concentration soil) were also resuspended and analyzed.

Elemental Analysis. House dust sample element concentrations were obtained using a Kevex 0700/8000 energy dispersive XRF spectrometer, calibrated with thin film standards prepared by Micromatter Co. (Deer Harbor, WA) (22). Accuracy was verified by analysis of NIST thin glass film XRF standards. A quality control standard was analyzed with each analytical run of up to 15 samples. Table 1 shows percent mass concentrations for 17 species for which element concentration exceeded twice the measurement uncertainty for more than half the samples. Concentration uncertainties were reported as 1 standard deviation error estimates propagated from the analytical measurement uncertainty (22). Mass and XRF measurement precision were calculated from replicate measurements performed every tenth sample. Total carbon content for six coarse fraction house dust samples was obtained using a thermal/optical reflectance carbon analysis system (23). Blank filters of the same lot number as the analyzed samples were used for background correction for both element and total carbon concentrations.

Proximate Source Media Sample Collection and Analysis. Site-specific source profiles of proximate source media were developed for soil, street dust, and indoor air samples collected in Jersey City. Samples were collected using protocols developed for CLEARS (20). A representative subset of yard soils ($n = 6$) and street dusts ($n = 7$) samples collected from study homes during the summers of 1992 and 1993 was used to create soil and street dust source profiles (25). Twenty-four hour indoor air samples ($n = 8$) were collected in during the summer of 1992. Due to difficulties in obtaining, processing, and analyzing sufficient quantities of dried paints from Jersey City, paint source profiles were developed from analysis of SRM material 1579 (certified Pb concentration 11.89%) and six pre-1960 interior lead-based paints in their original containers provided by Dr. Eugene Hall of Rutgers University Chemistry Department.

Soils and street dust samples were dried at room temperature then sieved to <500 μm to remove rocks and litter. To improve XRF quantitation it was desirable to maintain the same particle size range for all samples; therefore, samples were ground to uniform particle size in analytical grade methanol using a micronizing mill (Model 4000, Chemplex Industries, Inc., Eastchester, NY). After drying, the resulting powdered soils and street dusts had maximum particle sizes of 10 μm (25). Powdered samples were individually resuspended in a closed Plexiglas chamber attached to a fluidized bed generator containing three open-faced 37 mm filter cassettes (26). Each cassette held a preweighed Teflon filter (Gelman Sciences R2PJ037, Ann Arbor, MI) and was connected to pump pulling chamber air through the filter at 10 L/min. Mass loadings ranged between 0.5 and 2.5 mg of soil or street dust spread uniformly across the filters. After weighing, loaded filters were lightly coated with artist's fixative (Krylon Workable Fixative No. 1306, ~1 mg/filter) to minimize sample loss during XRF analysis.

TABLE 1. Average Elemental Concentrations and Measurement Uncertainties in the Coarse and PM$_{10}$ Size Fraction of House Dusts Collected in Jersey City, NJ ($n = 64$ for Coarse Fraction; $n = 61$ for PM$_{10}$ Fraction)

	coarse fraction				PM$_{10}$ fraction			
element	average (% mass)	unc^a (σ)	max value	number^b >2σ	average (% mass)	unc (σ)	max value	number >2σ
Al^c	1.4461	0.4494	3.1772	64	2.2446	0.6949	6.1154	61
Si^c	5.3318	1.7439	10.3531	64	7.3978	2.4192	15.2612	61
P^c	0.1513	0.0752	1.8059	41	0.2382	0.1165	3.0667	43
S^c	2.2041	0.1638	12.2915	64	3.3821	0.2569	16.7758	61
Cl	1.9622	0.5816	4.2979	64	2.2111	0.6592	6.1349	61
K	0.9730	0.2032	1.5956	64	1.2320	0.2586	2.3375	61
Ca	3.8118	0.7430	14.2085	63	5.6028	1.0771	22.6843	61
Ti^c	0.2175	0.0508	0.5432	58	0.2759	0.0623	0.7490	57
Mn^c	0.0176	0.0034	0.0476	63	0.0228	0.0043	0.0636	59
Fe^c	0.9846	0.0739	2.5270	64	1.2659	0.0974	3.0155	61
Ni	0.0073	0.0019	0.0260	54	0.0089	0.0025	0.0341	50
Cu	0.0226	0.0027	0.0895	64	0.0252	0.0032	0.1089	61
Zn	0.1824	0.0138	0.8065	64	0.2223	0.0173	0.9153	61
Br^c	0.0054	0.0020	0.0620	38	0.0061	0.0026	0.0679	31
Sr	0.0133	0.0023	0.0430	63	0.0173	0.0029	0.0606	59
Zr	0.0384	0.0044	0.1824	62	0.0627	0.0065	0.3445	61
Pb^c	0.0857	0.0091	0.2404	64	0.1133	0.0119	0.3122	60
total	17.46				24.33			

^{a} Mean of propagated measurement uncertainties for each sample, which takes into account error associated with XRF and gravimetric measurements. ^{b} Number of samples with concentration greater than twice the measurement uncertainty. ^{c} CMB fitting species used in the initial model solution, i.e., mean concentration of all samples in each size fraction.

Aliquots of six lead-based paints were thinned by adding two laboratory spatulas (5−10 g) of wet paint to 60 mL of methylene chloride. The resulting mixture was injected into an aerosol generator using a syringe pump (Harvard Apparatus Inc., Model 906, S. Natick, MA). The aerosol was directed into a Plexiglas chamber containing two open-faced 37 mm filter cassettes containing preweighed Teflon filters. Each paint aerosol was sampled until a uniform loading of approximately 2 mg/filter was obtained.

Multielement analyses of all source media were performed using NERL's Kevex 771 energy dispersive XRF system. Calibration of the spectrometer was performed using vacuum-deposited metal film and polymer film standards (27). Total uncertainty in measured concentrations were calculated from the propagated analytical measurement uncertainty (28). Blank filters of the same lot number as the analyzed samples were used for background correction. NIST SRMs 1579, 2709, and 2711 were ground, resuspended, and analyzed as part of the quality assurance program. Correction factors based on the measured concentrations obtained for NIST SRMs 2709 and 2710 were applied to the soil and street dust source profiles to adjust for signal attenuation due to use of the artist's fixative (25).

Data Analysis. Version 7 of the CMB receptor model (14) was used to apportion both particle size fractions using a process similar to EPA application and validation protocol developed for air pollution applications (29). The primary results of interest in this study were source-specific Pb contributions, expressed as percent of HD$_{Pb}$ from LBP$_{Pb}$, CR$_{Pb}$, and AIR$_{Pb}$. In theory, the mass from all sources should total 100%, but since the numerator is the calculated mass, this number varies with the uncertainty in both source and receptor measurements and the overall quality of model fit. The accuracy of the fractional contributions to HD$_{Pb}$ were evaluated by examining several model fit indices, including TSTAT, R^2, χ^2, source contribution estimates (SCEs), and normalized residuals ratios (13). In addition, CMB's similarity/uncertainty clusters (S/U clusters) diagnostic algorithm indicates when two or more source profiles may be collinear. Strongly collinear profiles can propagate large uncertainties in SCEs and in source-specific fractional Pb contributions to HD$_{Pb}$. The model also has diagnostics that indicate the most influential element in each source profile, based on the

normalized modified pseudo-inverse matrix (MPIN). MPIN results were used to perform sensitivity analyses by systematically removing the most influential element for each source profile and recalculating the model.

Results and Discussion

Element Concentrations in House Dust. Mean percent concentrations of 17 elements in the coarse and PM$_{10}$ size fractions of Jersey City house dust are presented in Table 1. Also shown are the measurement uncertainty and the number of samples for which the elemental concentration exceeded the quantifiable limit, i.e., twice the measurement uncertainty. The average HD$_{Pb}$ concentration in the coarse fraction was 0.0857 ± 0.0091% (857 ± 91 μg/g). The crustal elements Al, Si, S, Ca, Cl, K, and Fe had the highest concentrations, and measurable quantities of some metals commonly found in both lead-based paints and crustal sources, such as Ti and Zn, were also present in most samples. Ba, an element sometimes found in high concentration in lead-based paints, was below detection in 61 of the 64 samples (25). The total mass of the 17 elements listed was 17.5%. The unaccounted mass is assumed to be largely comprised of organic and inorganic carbon compounds, oxygen, hydrogen, and other low atomic number ($Z < 13$) elements not quantified by XRF.

PM$_{10}$ size fraction elemental concentrations were obtained for 61 of the 64 samples; resuspension mass loadings for three samples were too low for accurate XRF quantitation. The mean HD$_{Pb}$ concentration in these samples was 0.1133 ± 0.0119% (1133 ± 119 μg/g), higher than the mean concentration in the coarse fraction. Crustal and paint-associated element concentrations followed a pattern similar to that observed for the coarse fraction, but a larger proportion (24.3%) of total mass was accounted for by the 17 measured elements.

Initial Solution and Optimization of Source Profiles. The CMB application and validation protocols followed the seven step process by Pace and Watson (29). To test model applicability, a series of tests, shown in Table 2, were performed on mean dust concentration values in the coarse size fraction using the source profiles shown in Table 3. Initial fitting species for the "best fit" trial shown in Table 2 was obtained using the elements Al, Si, P, S, Ti, Mn, Fe, Br, and Pb, and source profiles representing indoor air (AIR2), lead-

TABLE 2. Sensitivity of Coarse Fraction House Dust Lead CMB Source Contribution Estimates to Changes in Source Profiles

source profile	best fit % Pb from source	TStat[a]	trial 1 % Pb from source	TStat	trial 2 % Pb from source	TStat	trial 3 % Pb from source	TStat	trial 4 % Pb from source	TStat	trial 5 % Pb from source	TStat	trial 6 % Pb from source	TStat	trial 7 % Pb from source	TStat
AIR			31.3	7.38	30.7	7.42										
AIR2	18.9	7.44					19.0	7.45	18.9	7.45	18.8	7.39	19.0	7.46	19.0	7.46
P1579	39.8	3.05	15.3	0.85	27.1	2.03					137.0	1.06	14.8	0.72		
PHITI							34.9	3.39					25.5	1.55	26.4	1.72
PHIPB									37.7	3.00	−95.0	−0.75			13.8	0.74
CRUSTAL	42.1	6.66	69.1	2.55	43.2	6.94	41.1	6.48	43.4	7.00	39.7	5.59	40.5	6.32	40.8	6.40
STREET			−15.1	−0.97												
sum % Pb	100.8%		100.6%		101.0%		95.0%		100.0%		100.5%		99.8%		100.0%	
CMB Model Diagnostics																
df[b]	6		5		6		6		6		5		5		5	
χ^2 [c]	0.56		0.5		0.59		0.24		0.65		0.55		0.19		0.18	
R^2 [d]	0.99		0.99		0.99		0.99		0.99		0.99		0.99		0.99	
CLUSTERS[e]			SOIL STREET								P1579 PHIPB SOIL					

[a] TStat: the ratio of the source contribution estimate (SCE) to the standard error of the estimate. [b] df: degrees of freedom in the model, equal to the number of fitting species minus the number of sources. The fitting species using in all model runs presented on this table are Al, Si, P, S, Ti, Mn, Fe, Br, and Pb. [c] χ^2: measure the agreement between calculated and measured concentrations. The closer χ^2 is to zero the better the model fit. [d] R^2: measures the correlation between calculated and measured concentrations. [e] CLUSTERS: similarity/uncertainty (S/U) clusters which identify the potential for collinearity among the profiles that are contained in a CLUSTER. When source profile mnemonics (see text for definitions) are listed, they appeared together in one or more clusters and are probably collinear.

TABLE 3. Multielement Concentrations and Measurement Precisions in the Air (AIR2), Lead-Based Paint (P1579, PHITI, and PHIPB), and Soil (CRUSTAL) Source Profiles[a]

| | AIR2 | | P1579 | | PHITI | | PHIPB | | CRUSTAL | |
element	conc (%)	unc[b]	conc (%)	unc	conc (%)	unc	conc (%)	unc	conc (%)	unc
Al	0.7747	0.2806	3.1189	0.9492	<0.0001	0.0311	<0.0001	0.0396	8.4563	1.6257
Si	2.0972	0.4983	12.6873	4.0915	0.5380	0.1206	0.1525	0.1015	29.0816	4.5085
P	0.1604	0.0409	<0.0001	0.1173	<0.0001	0.0128	<0.0001	0.0163	0.1772	0.0159
S	4.9136	0.5868	2.3391	0.4124	2.1883	0.1516	<0.0001	0.6191	0.1410	0.0119
Cl	0.2440	0.0328	<0.0001	0.2443	<0.0001	0.0124	<0.0001	0.0944	0.0158	0.0040
K	0.6630	0.0932	0.8743	0.1815	0.0136	0.0062	0.0107	0.0065	1.8967	0.1301
Ca	1.3643	0.1682	5.1071	0.9352	<0.0001	0.2837	0.0404	0.0090	1.5575	0.0743
Ti	0.0627	0.0144	4.5129	0.4251	5.4620	0.3443	0.0055	0.0179	0.7818	0.0369
Cr	0.0044	0.0019	0.0198	0.0448	0.1307	0.0075	3.3103	0.1659	0.0258	0.0025
Mn	0.0166	0.0030	0.4025	0.0300	0.0197	0.0016	0.0038	0.0036	0.0826	0.0040
Fe	0.8869	0.1181	2.0519	0.1482	0.0795	0.0044	0.0161	0.0017	4.8871	0.1840
Co	0.0018	0.0045	0.0051	0.0310	0.0061	0.0007	0.0022	0.0006	<0.0001	0.0009
Ni	0.0374	0.0063	<0.0001	0.0047	<0.0001	0.0007	<0.0001	0.0008	0.0005	0.0006
Cu	0.0362	0.0059	0.2029	0.0148	<0.0001	0.0016	0.0204	0.0017	0.1077	0.0045
Zn	0.1136	0.0156	6.7987	0.4902	1.2053	0.0858	0.0217	0.0030	0.0820	0.0053
Br	0.0101	0.0024	<0.0001	0.0956	<0.0001	0.0006	0.0066	0.0022	0.0007	0.0005
Sr	0.0070	0.0023	0.0939	0.0077	0.0505	0.0042	<0.0001	0.0021	0.0114	0.0015
Zr	0.0042	0.0074	0.0126	0.0039	<0.0001	0.0013	<0.0001	0.0027	0.0763	0.0046
Pb	0.0366	0.0067	12.9831	0.9363	1.3646	0.0688	15.1691	0.7593	0.2840	0.0123
total	11.43		51.21		11.06		18.76		47.67	

[a] All concentration values in percent mass. [b] Mean of propagated measurement uncertainties for each sample, which takes into account error associated with XRF and gravimetric measurements.

based paint (P1579, NIST SRM 1579), and soil (CRUSTAL). Using these elements and profiles, it was possible to obtain CMB performance indices in the range specified by Pace and Watson (29), i.e., $R^2 > 0.95$, $\chi^2 < 1.0$, TSTAT ≥ 2.0, and normalized residuals ratios < |2.0|. None of these three profiles were collinear, as indicated by the lack of an S/U cluster. MPIN diagnostics indicted that, for the best fit solution shown in Table 2, the most influential elements were S for AIR2, Pb for P1579, and Fe for the CRUSTAL source profile.

Table 2 also demonstrates the sensitivity of the observed results to changes in individual source profiles. In trial 1, CMB's diagnostic algorithm showed a S/U cluster between the CRUSTAL and street dust (STREET) source profiles. This collinearity was manifested by a negative TSTAT and a physically impossible Pb source contribution from street dust (−15.1%). This means that these two sources could not be distinguished using these profiles because there were no unique relative ratios between the elements used in the model fit. Without additional information to distinguish these two sources, the model provides best results using the CRUSTAL source profile alone. These results are consistent with past studies showing that street dusts are 60−90% soil (3).

Trials 1 and 2 indicated that the AIR source profile, which is the average of 8 days of indoor air monitoring, resulted in an AIR_{Pb} of >30%. Examination of the monitoring data upon which the profile was based indicated that 1 of the 8 days had airborne Pb concentrations 1 order of magnitude higher than the remaining 7 days. High concentration on a single day is likely indicative of an intermittent source, so a separate profile was created that comprised a single day's monitoring (AIRHIPB). A modified profile, AIR2, was also created using the average elemental concentrations of the remaining 7 days. Inclusion of both these profiles in a model solution resulted in a S/U cluster, so the AIR2 profile alone was used in analysis

TABLE 4. Percent Contribution to HD$_{Pb}$ from AIR$_{Pb}$, LBP$_{Pb}$, and CR$_{Pb}$ Source Pathways and Results of Sensitivity Analysis Performed by Systematic Removal of the Most Influential Element in Each Source Profile and Subsequent Model Recalculation

	coarse fraction			PM$_{10}$ fraction		
	AIR$_{Pb}$[a]	LBP$_{Pb}$[b]	CR$_{Pb}$[c]	AIR$_{Pb}$	LBP$_{Pb}$	CR$_{Pb}$
			Best Fit Results			
mean	17.2%	34.5%	49.3%	17.7%	33.9%	49.7%
std dev	16.0%	19.4%	24.0%	17.1%	20.8%	25.2
range	0−78.6%	0−77.8%	0−98.6%	0−81.4%	0−79.9%	0−95.6%
			Results Obtained after Removing Most Influential Species (Usually S) from the AIR2 Source Profile			
mean	19.4%	35.8%	46.0%	17.0%	34.7%	49.5%
std dev	11.7%	19.3%	20.2%	14.9%	20.6%	22.3%
range	0.2−53.5%	0−78.1%	10.2−97.8%	0−70.9%	0−79.4%	1−101%
			Results Obtained after Removing Most Influential Species (Usually Pb) from the Paint Source Profiles			
mean	17.3%	32.8%	51.2%	24.1%	36.7%	49.4%
std dev	16.2%	20.7%	23.1%	23.7%	26.9%	27.9%
range	0−79.3%	0−76.4%	0−100%	3.1−100%	0−103.1%	0−97.7%
			Results Obtained after Removing Most Influential Species (Usually Fe) from the CRUSTAL Source Profile			
mean	17.9%	35.0%	48.2%	18.2%	29.8%	53.5%
std Dev	18.4%	19.8%	25.4%	18.5%	21.9%	26.2%
range	2.9−77.9%	0−79.8%	0−99.7%	0−91.2%	0−79.4%	0−105.4%

[a] AIR$_{Pb}$: calculated percent Pb from airborne sources using AIR2 source profile. [b] LBP$_{Pb}$: calculated percent Pb from paint sources using either P1579, PHITI, or PHIPB source profile. [c] CR$_{Pb}$: calculated percent Pb from crustal sources using CRUSTAL source profile.

because that profile was considered most representative of indoor air sampled for this study. Use of AIR2 resulted in a decline of AIR$_{Pb}$ to approximately 19% of HD$_{Pb}$. AIR2 was used in most of the remaining model runs because the frequency of the possible intermittent source represented by the AIRHIPB source profile was not known.

Trials 3−7 demonstrate that use of any of three lead-based paint profiles or the inclusion of more than one paint profile resulted in small changes in LBP$_{Pb}$. The three lead-based paint source profiles used in model runs were developed to account for the variability in Pb and other element concentrations in interior lead-based paints (25). Older paints had concentrations of up to 50% Pb, while later paints had lower Pb concentrations but increased concentrations of Ti, Zn, and Ba (5). Trials 3 and 4 use PHITI and PHIPB, respectively, both of which were uniquely different from P1579. PHITI was a composite of three paints, all of which had higher Ti than Pb concentrations, and much lower Si, Al, Fe, and Zn levels compared to P1579 (Table 3). The PHIPB profile is comprised of a single paint, had the highest Pb (15.2%) levels, and lower levels of Al, Si, S, Ti, and Fe compared to P1579. Results of trials 3 and 4 indicate that PHITI and PHIPB profiles fit the data nearly as well as P1579, but with either a lower TSAT, in the case of PHIPB, or larger normalized residuals, in the case of PHITI. Trials 5−7 show that adding a second lead-based paint profile resulted in collinearity among profiles (trial 5) or decreases in TSTAT values for the paint source profiles to less than 2.0 (trials 6 and 7). A TSTAT less than 2.0 indicates that the precision of the SCE is less than twice its standard error. Inclusion of more than one paint profile decreases the precision but does not change the magnitude of LBP$_{Pb}$. Therefore, the simpler single paint source profile model solution was used.

Model Results for Individual House Dust Samples. The initial results for coarse fraction CMB calculation values indicated that the model could resolve three source pathways using the CRUSTAL, AIR2, and any one of three lead-based paint source profiles. On the basis of these initial tests, individual dust samples from both the coarse and PM$_{10}$ fractions were apportioned using the source profiles in Table 3. AIR2 and CRUSTAL were included in each model run, and the lead-based paint profile (either P1579, PHITI, or PHIPB) that optimized CMB diagnostics and minimized normalized residuals was included. The fitting elements used in most CMB model runs on individual dust samples are

indicated in Table 1, with the occasional addition of other elements from Table 1 if their normalized residuals were <|2.0|. As with the initial trials, some elements with high concentrations and good measurement precision in both source media and dust were often excluded from model fit, e.g., Cl, K, Ca, Ni, Cu, Zn, Sr, and Zr, because their presence resulted in model diagnostics and normalized residuals outside of their target range. All these elements except Sr and Zr have been shown to be enriched in house dusts in comparison to soil (3). The elements Cl, K, and Ca are likely of crustal origin, but can also come from plaster or cement (Ca) or road salt (Cl) (12). The metals Ni and Cu are associated with corrosion of metallic parts, while Zn has numerous potential sources besides lead-based paints, including weathered galvanized surfaces, linoleum, and various rubber products, including automobile tires and carpet backing (3). Since Pb is not commonly present in high concentrations in any of these other sources, exclusion of these elements presumably does not bias the HD$_{Pb}$ mass balance calculations.

Mean percent source contributions (i.e., AIR$_{Pb}$, CR$_{Pb}$, and LBP$_{Pb}$) of the AIR, CRUSTAL, and paint source profiles to HD$_{Pb}$ in the coarse and PM$_{10}$ size fractions of are shown in Table 4. Also shown are results of a sensitivity analysis examining the effect of removing the most influential element from each source profile. Under the best fit scenario, the CMB model resolved sources into 2 or 3 contributing pathways for 61 individual coarse fraction samples. The remaining three samples all had relatively low HD$_{Pb}$ concentrations (110, 300, and 390 μg/g) and element profiles that were so similar to a single profile, either CRUSTAL or AIR2, that no mass balance could be performed. For the coarse size fraction, CR$_{Pb}$ was the largest contributor to HD$_{Pb}$, with a mean value of 49.3 ± 24.0% and a range of 0−98.6% (Table 4). LBP$_{Pb}$ had a mean contribution to HD$_{Pb}$ of 34.5 ± 19.4%, and a range of 0−77.8%. AIR$_{Pb}$ was the smallest contributor to HD$_{Pb}$, with a mean value of 17.2 ± 16.0% and a range of 0−78.1%. The source contributors to the PM$_{10}$ particle size fraction were similar to those observed for the coarse particle size fraction, with mean contributions of 49.7 ± 25.2% (range 0−95.6%), 33.9 ± 20.8% (range 0−79.9%), and 17.7 ± 17.1% (range 0−81.4%) for CR$_{Pb}$, LBP$_{Pb}$, and AIR$_{Pb}$ source pathways, respectively (Table 4).

Stability of Model Results. Stability of model results were assessed by recalculating model outputs after excluding the most influential element in each source profile (29). For

both size fractions, (1) S was the most influential element in the AIR2 source profile for more than 95% of the dust samples; (2) Pb was the most influential element for the paint source profile (either P1579, PHIPB, or PHITI) for >90% of the dust samples, while Ti was the most influential element in the remaining cases; and (3) Fe was the most influential element in the CRUSTAL source profile for >85% of the dust samples, while S was the most influential element for the remaining samples.

Removal of the most influential element had a negligible effect on model statistics and on average model results in most cases, but the source-specific percent lead contributions changed substantially for some dust samples. Removal of the most influential element (usually Pb) in the paint source profile from the model fit decreased LBP_{Pb} by <2% for coarse fraction samples. Mean fractional pb contributions were $51.2 \pm 23.1\%$ (range 0−100%), $32.8 \pm 20.7\%$ (range 0−76.4%), and $17.3 \pm 16.2\%$ (range 0−79.3%) for CR_{Pb} LBP_{Pb}, and AIR_{Pb} sources, respectively (Table 4). Removal of Pb, however, had a major effect on the model's ability to resolve sources with this set of profiles: it resulted in S/U clusters for 26 of the 61 samples, usually between the CRUSTAL and one of the paint source profiles. As a consequence, the average results reported in Table 4 are based on only samples for which no collinearity existed, i.e., the 35 remaining samples. For the coarse size fraction, removal of S from the model fit increased average AIR_{Pb} from AIR2 by a little more than 2% and decreased the magnitude of the range; removal of Fe from the model fit decreased average CR_{Pb} from this source pathway by a little less than 1% and had no effect on the range of observed values. Sensitivity analysis results for the PM_{10} fraction indicated that results were also relatively stable, with LBP_{Pb} and CR_{Pb} source contributions increasing slightly with the removal of Pb and Fe, respectively, from the model fit (Table 4). In general LBP_{Pb}, CR_{Pb}, and AIR_{Pb}, fractional contribution estimates were relatively robust to removal of the most influential elements for both particle size fractions. This series of tests demonstrates the value of using multi-element source profiles and CMB analysis, rather than a single element tracer, to identify and quantify source contributors.

Compliance with Assumptions and Limitations of the CMB Method. Confidence in CMB results is contingent on compliance with the six basic assumptions of the CMB model (*14*). Assumption 1, that composition of source emissions are constant over time, can never be fully met, because of variability in air, paint, and crustal source profiles over time, season, and home analyzed. Of greater importance, however, is that the profiles used in this study be *representative* of the source pathways impacting the homes where dust samples were collected. The air and crustal profiles are likely to be representative because they were developed from local Jersey City samples. It might be argued that the indoor air samples were collected only over one season (summer of 1992) whereas dusts collected in carpets may reflect long-term deposition of airborne particles, hence past airborne Pb levels when leaded fuels were still in use. We think it is more likely, however, that the carpets dust collected in this study is comprised of more recent deposition, tracking of soil, and flaking of lead-based paints since most individuals clean their homes periodically. Higher past airborne Pb concentrations would be expected to increase the fractional AIR_{Pb} contribution. An upper bound estimate is likely approximated by the ∼30% AIR_{Pb} contribution calculated when using the AIR source profile (Table 2).

While the paint profiles were not developed from local samples due to difficulties in obtaining and analyzing sufficient quantities of Jersey City lead-based paints, the profiles developed for this study are likely representative of the paints used in these homes. Furthermore, the sensitivity analysis presented in Table 2 showed that the LBP_{Pb} contribution changes only slightly when PHITI or PHIPB is substituted for P1579. The LBP_{Pb} contribution changes little between profiles because the SCE for the profiles with higher Pb concentrations decreases.

CMB assumptions 2 (non-reactivity of chemical species), 3 (all significant Pb sources identified and characterized), 4 (linear independence of source composition), and 5 (number of sources or source categories greater than the number of chemical species) are essentially met with the following three qualifications. (a) We have identified and characterized the major proximate sources that contribute to HD_{Pb} but not the primary emission sources. The CMB method as used in this paper distinguishes HD_{Pb} contributions from proximate media such as crustal, airborne, and lead-based paint sources, but does not reveal contributions form the ultimate sources that contribute to the airborne and crustal categories. (b) Evidence for linear independence of the source compositions is shown by the lack of S/U clusters between AIR2, CRUSTAL, and any of the three paint profiles used. To meet this requirement, however, it was necessary to replace two sources with similar composition, soils and street dusts, with the single CRUSTAL (soil) profile. (c) Less than 50% of the mass of the source and receptor (dust) samples was characterized: the unaccounted mass is assumed to be primarily oxygen, hydrogen, organic compounds, and other elements with atomic number <13. Previous studies have shown that the organic content of house dust is approximately 40% (*30*). Analysis of six Jersey City house dust samples indicated that the total carbon content of these dusts averaged 20% (range 13−22%). Since all major source contributors to HD_{Pb} appear to have been accounted for, however, the mass balance performed with Pb and the eight other elements indicated in Table 1 is valid.

Compliance with assumption 6, that measurement uncertainties are random, uncorrelated, and normally distributed, is difficult to assess in any study. The effect of deviations from this assumption has not been extensively studied. Nonrandomness and correlation among measurement errors would result in biases in the calculated concentrations with respect to measured concentrations. Measurement errors are likely log-normally distributed, and the variability associated with the measurements is likely less than the within-media variability. Quality assurance testing of both source and receptor media and comparison of these results with data from other CMB studies and source profile libraries indicates that reported values are representative of their source media (*12, 31*). Since source profile samples for crustal and air are Jersey City specific and model outputs are relatively insensitive to substitution of different paint source profiles, it is likely that developing additional profiles with larger sample sizes or different data sets will result in only small increases in the precision of the LBP_{Pb}, CR_{Pb}, and AIR_{Pb} contribution estimates.

Consistency with Other Sources Apportionment Methods. There are two studies that have developed quantitative source contribution estimates for urban HD_{Pb}. A study in Christchurch, New Zealand, homes developed quantitative estimates by comparing dust lead concentration data from six homes with lead-based paints to newer homes without leaded paints (*30*). It concluded that 45% of HD_{Pb} came from paints, 3-5% from soil, 15−20% from street dust, and 15−25% from settled aerosols. Hunt and co-workers performed studies using SEM-EDX and a cluster analysis approach on dusts from 16 households in London, England (*4, 8*). They concluded that road dusts were the largest source of HD_{Pb} particles <64 μm, contributing 20−65% of total Pb; paints and soils were the next largest sources, contributing 20−80% and 10−30% of total Pb particles, respectively. If classified by particle volume instead of absolute particle number, the average contribution from paint increased by

approximately 7%, with a reduced contribution from road dust and garden soil of 8 and 1%, respectively.

These two studies used different source groupings than this study. The first (30) showed that paint > air ≈ crustal sources, while the second (4, 8) showed that road dust > paint > soil. Both show, however, that external source pathways, i.e., crustal and airborne Pb, are at least as large as direct contributions from paint, though none of these studies distinguish interior versus exterior lead-based paints. Our results show that on average, crustal > paint > air, and are consistent with past results in showing that exterior sources can contribute a large proportion of the HD_{Pb} particles. Our study was performed on dusts from a much larger number of homes, however, and suggest that (1) sources of HD_{Pb} vary considerably among homes and (2) sources contributing to the overlapping coarse and PM_{10} fractions do not vary substantially within homes. CMB modeling provided robust estimates for a large number of samples that can be generalized to urban environments with similar sources.

Our results compile Pb source contributions by proximate source, not initial emitter. The Pb contribution from air probably results primary from outdoor activities that resuspend crustal sources as well as direct emission from industrial and mobile sources. It may also represent human activities that resuspend dust indoors, such as vacuuming and sweeping. Indoor air Pb concentrations measured in this study were much lower than current ambient standards. Nevertheless our results indicate that this source contributes significantly to HD_{Pb} levels over time. Outdoor Pb sources, i.e., both aerosol deposition and tracked-in soils and street dusts, contribute approximately two-thirds of the HD_{Pb} mass. Our results do not determine the original source of these Pb particles, but do suggest that reduction of these two major source pathways and removal or stabilization of interior lead-based paints would both significantly contribute to reductions in lead exposure in urban preschool children.

Acknowledgments

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