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Application of Receptor Modeling to Indoor Air Emissions from Electroplating

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In work areas containing multiple sources of the same air pollutant, it is useful for control purposes to be able to separate out the contribution from each individual source. In this study, the chemical mass balance (CMB) receptor model was used to allocate the contributions from multiple sources to area concentration measurements in three electroplating shops. Shop 1 was a room with a single copper electroplating line; shop 2 was a large bay containing a chromium conversion coating line, a continuous chromium electroplating line, and several manual electroplating operations; shop 3 contained a piston chrome plating line, a decorative chrome plating line, and manual and barrel zinc coating lines. Hourly area concentrations of the composition of particulate matter were collected at a number of locations in each workroom. Activities of individual sources within each room were observed and recorded over each 1-hour interval. The receptor modeling approach uses the elemental composition of one or more source categories to determine what fraction of an area sample is contributed by each source. In most cases the CMB model predicted over 90 percent of the measured concentrations. The allocation procedure explained 100 percent of the copper measured at three locations in shop 1, with contributions of 95 to 98 percent from the plating line and the rest from air outside the room. Copper concentrations contributed from plating were consistent with the emission rates determined by other methods. For shop 2, a two-source model explained 100 percent of the chromium measured at five sampling locations. Chromium residuals at two other locations were related to manual line activities not included in the model, which were also likely to involve chromium emissions. For shop 3, the percent contributions of chromium from the piston plating line and the decorative plating line were consistent with distance from each of the sources. Piston line contributions were also consistent with emission rates. Based on these findings, the CMB model is a useful method for allocating specific source contributions to area concentration measurements in spaces containing multiple sources, and the same approach could also be applied to personal samples. WADDEN, R.A.; LIAO, S.-L.; SCHEFF, P.A.; FRANKE, J.E.; CONROY, L.M.: APPLICATION OF RECEPTOR MODELING TO INDOOR AIR EMISSIONS FROM ELECTROPLATING. APPL. OCCUP. ENVIRON. HYG. 13(12):829–838; 1998. © 1998 AIH.

Indoor air quality is largely determined by the emission rate of contaminants from indoor sources and the ventilation air available to dilute and remove the pollutants. Control depends on restricting the release of contaminants into the work space. For indoor spaces containing only one source, the relationship between source release and concentration is relatively straightforward. But for spaces that contain more than one source, the situation is more complex. Knowing specific source contributions to air contaminants in a work space containing multiple sources provides useful information for effective indoor pollution control.

The chemical mass balance (CMB) receptor model is a method used to quantitatively allocate the source contributions of individual sources to ambient receptor concentrations in the presence of multiple sources. The method depends on emissions from each source having a unique pattern of chemical compositions (i.e., having a chemical fingerprint). The chemical components that make up the fingerprints are referred to as fitting compounds or fitting elements. The differences between fingerprints are used to determine the contribution of each source to an area (receptor) sample. The application and evaluation of the CMB model to outdoor particulate matter and gaseous pollutants have been widely studied.(1–8) However, only recently has the model been applied in indoor industrial settings.(9,10)

In this study the CMB model was used to allocate the contributions from multiple sources to area concentration measurements in three electroplating shops. Shop 1 was a room with a single copper electroplating line;(11) shop 2 was a large bay containing a chromium conversion coating line, a continuous chromium electroplating line, and several manual electroplating operations;(12) and shop 3 contained a piston chrome plating line, a decorative chrome plating line, and manual and barrel zinc coating lines.(13) For each shop, two or three sources were selected for applying the CMB model. The chemical composition of workroom emissions (i.e., source fingerprint) was determined for each source on an hourly basis, and for one shop, also on a 6-hour basis. In each case, data were available from previous field tests, although these had been carried out for purposes other than application of the CMB model.(11–13)

The advantage of applying the CMB approach is that if the contributions of different sources of the same contaminant, such as chromium, are separable, it is possible to determine which source makes a bigger contribution to a particular area concentration and therefore presumably requires more control. The same technique is also applicable to personal exposure measurements. Our interest in this study was (1) to determine the chemical compositions of emissions from various indoor sources (i.e., source fingerprints); (2) to evaluate whether such fingerprints were different enough from each other to separate the contributions of each source; and (3) to apply multiple source CMB models to allocate the contributions to area samples collected in the space. We also used source activities and source emission rates determined by independent methods to check the consistency of the allocation results.

Methods

The CMB Model

The basic assumptions for the CMB model are that the concentration of element i at the receptor location equals the sum of the contributions to i from j sources, and that the mass is conserved. No prior assumptions about source location and strength, air mixing, or flow direction are required.(1) The general mathematical equation is given by

$$Y_i = \sum_{j=1}^{N} \beta_j Z_{j,i} + E_i \qquad (1)$$

where:

Y_i = the measured concentration of fitting element i at the receptor site with units of micrograms of i per cubic meter of air
$Z_{j,i}$ = the chemical composition of source j for element i with units of micrograms of i per microgram of receptor particle mass
β_j (the unknown) = the micrograms of receptor particle mass per cubic meter of air, measured at the receptor site, allocated from source j
E_i = the residual term which is the difference between the measured and predicted concentration for element i

The summation is over the total number of sources, N. For our application the "micrograms of receptor particle mass" is the sum of the fitting element masses at the receptor for a particular measurement period.

Equation 1 is individually written for each fitting element or chemical component. Although Y_i and $Z_{j,i}$ are different for each fitting element, each equation contains the same unknowns, β_j, the source coefficients. As long as there are more fitting elements than sources, the set of elemental mass balance equations can then be solved for the values of β_j. After the β_j's have been determined, they can be substituted back into Equation 1 to calculate an estimated value, $\hat{Y}_i$. The difference between Y_i and $\hat{Y}_i$ is the residual composition, E_i, not explained by the model. If the estimated amounts are consistently less than those measured, this positive residual value may imply the presence of a significant, but previously unrecognized and unmodeled, source.

For each area sample, the set of equations (Equation 1), one for each fitting element, was solved for β_j by applying least-squares regression. All chemical fitting elements should have equal influence on the solution, and if the concentrations of different elements are all within the same order of magnitude, this will be so. However, since concentrations between elements in a particular fingerprint may differ by several orders of magnitude, it is necessary to use a weighting factor to ensure that each element equally influences the determination of β_j. The weights used were the reciprocal of the measured concentration of each element squared $[1/(\text{conc}_i)^2]$ to give the low and high concentration elements equivalent effect in determining the solution. Any standard statistical package can be used to carry out the regression calculation (e.g., SAS,(14) SYSTAT,(15) etc.).

Site Descriptions, Measurements, and Fingerprint Development

Duct and area samples for all sites were collected on open-face 25-mm(13) or 37-mm(11,12) polycarbonate filters using calibrated flow rates of approximately 2 L/min. All filters collected from three shops were analyzed by proton-induced X-ray emissions (PIXE).

Unique source fingerprints are required to apply the CMB model. Source fingerprints consist of fitting elements. Elemental concentrations in source emissions or area (receptor) samples that were above detection limits (and above blank filter concentrations) were chosen as fitting elements. Consequently the number of fitting elements was different for each shop. The fingerprint is the ratio of the specific elemental concentration of the source divided by the total particulate concentration of the source. We often did not have a reliable measure of total particulate, so the sum of the masses of fitting elements in each sample was used as a surrogate for total particulate. For concentrations below detection limits or elemental particulate mass less than filter background levels, zero was used in the calculation.

SHOP 1. This large room contained a single copper electroplating line, but was located in a building housing many other processes for the production of electronic components (Figure 1). The plating line consisted of 11 tanks, 10 of which were being used, and which were served by a push-pull ventilation system. Twelve 1-hour particulate samples were taken over 2 days at five sampling locations (A, B, C, D, and E). The two sources considered for this location were the plating operation itself and the air entering from outside the room.

Evaluation of source fingerprints for this shop was on an hourly basis, because fingerprints could be different for each hour depending on how a source was operated. Twelve area measurements in the hood of the ventilation system (at location D) were used as the fingerprint representing the plating line; the hourly area measurements at location E were used as the fingerprint representing air from outside the room. The hourly source fingerprints for the copper plating line and entering air are listed in Table 1.

SHOP 2. A large bay contained a hexavalent chrome conversion (chemical) coating line, a continuous decorative hexavalent chrome electroplating line, and several manual electroplating operations (which were only occasionally in use).(12) Figure 2 shows the location of each line and other components related to operations. The two chromium plating lines were adjacent to each other and were operated simultaneously. Hourly area concentrations were collected at three monitoring locations close to each line (marked as "edge," "near," and "far" in Figure 2). Six 1-hour samples were taken near the conversion coating line and four 1-hour samples were taken near the continuous line. In addition, one location was chosen

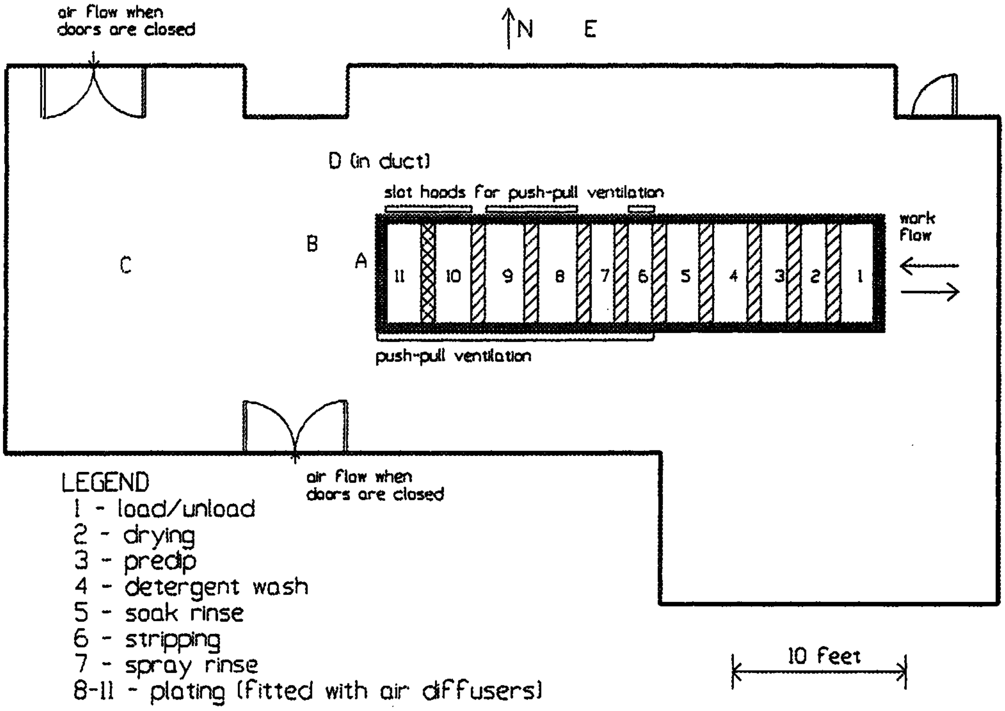

FIGURE 1. Plan view of shop 1 with sampling locations (A, B, C, D, and E).

on the opposite side of the conversion line chromium tank for three of the 1-hour sampling periods (marked as "opposite" in Figure 2).

The two plating lines were each served by a local exhaust ventilation system (LEV). Emission composition was characterized from a 1-hour measurement in the LEV duct on each line. Source activities were determined for all sampling periods.(12,16) The model applied to this space contained separate source terms for the conversion and the continuous lines. The LEV duct concentrations (one 1-hour measurement per line) were used as the fingerprints. Source fingerprints for the two plating lines are listed in Table 2.

SHOP 3. Four processes were operated in this shop, which was a single room within a much larger factory building containing many other operations. The processes were a piston plating line with hexavalent chromium electroplating tanks, a decorative trivalent chrome electroplating line, a manual zinc plating line, and a barrel zinc plating line (Figure 3).(13) The piston line was served by a LEV. The decorative line was also served by a LEV, but not on the chromium electroplating baths. The manual zinc line included one chromium-containing plating tank, and the barrel line contained two chromic acid tanks. Twelve simultaneous 1-hour samples were taken at each of six locations (A, B, C, E, F, and G) in the workplace and one

TABLE 1. Shop 1: Hourly Source Fingerprints (wt%)

		Hour											
Source	**Element**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Copper plating line	Si	3.1	5.1	1.3	4.8	0.0	0.3	0.0	1.3	2.9	1.5	0.3	1.6
	S	63.	60.	62.	59.	72.	67.	62.	68.	66.	67.	69.	68.
	Fe	2.9	0.3	1.4	1.3	1.6	0.6	7.0	1.6	0.8	0.5	0.6	0.8
	Ni	0.00	0.01	0.00	0.02	0.01	0.06	0.00	0.04	0.01	0.05	0.02	0.02
	Cu	31.	35.	34.	34.	23.	32.	31.	29.	29.	30.	30.	29.
	Zn	0.0	0.2	0.8	1.3	2.6	0.1	0.1	0.3	0.4	0.4	0.4	0.4
Entering air	Si	2.0	38.	29.	77.	35.	38.	2.5	20.	31.	20.	18.	18.
	S	84.	50.	57.	0.0	48.	48.	77.	66.	56.	74.	78.	70.
	Fe	7.4	11.	9.5	18.	16.	8.8	16.	11.	11.	3.8	3.4	8.0
	Ni	0.05	0.27	0.30	0.47	0.15	0.06	1.3	0.02	0.02	0.03	0.22	0.00
	Cu	0.5	0.5	0.3	1.1	0.7	1.5	0.2	0.2	0.2	0.2	0.3	0.1
	Zn	5.7	0.7	3.8	4.0	0.3	4.0	3.1	2.3	1.8	3.1	0.9	3.4

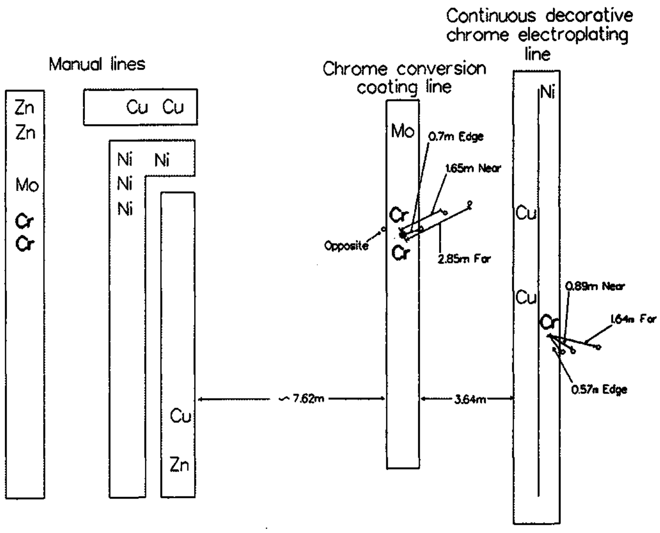

FIGURE 2. Plan view of shop 2 with sampling locations (elemental symbols indicate tanks containing these materials).

location in the ventilation duct (location D) of the piston line (Figure 3). Six-hour average concentrations were also determined for the air flowing into the room during the test periods at two locations (H and I). The energy used by each of the continuous plating processes was recorded concurrently with the concentration measurements.[13] Two different models were applied. One contained separate hourly fingerprints for both the piston and the decorative lines. The other, a three-source model based on 6-hour average concentrations, included a separate fingerprint for make-up air from the rest of the factory as well as fingerprints for each of the two lines.

The Two-Source Model. For the two-source CMB model, the two sources defined were the piston line and the decorative line, and source fingerprints were developed on an hourly basis. The 12 hourly concentration measurements in the LEV duct (sampling location D) of the piston line were used as the fingerprint for the piston line. Sampling location E at the edge of the chrome bath (0.61 m from the center of the bath) and F (1.2 m from the center of the bath) were close to the decorative line (Figure 3). A paired *t*-test was applied to the hourly elemental weight fractions of each of the fitting elements (chlorine, chromium, copper, iron, nickel, lead, sulfur, silicon, and zinc) at locations E and F. The difference used to perform the analysis was the difference of weight fraction for each element between E and F divided by average weight fraction of E and F at the same hour. The results showed on an element-by-element basis that the hypothesis (two means were equal) cannot be rejected (p value = 0.68). Therefore, the average elemental weight fractions of E and F were used as the fingerprint for the decorative line. The source fingerprints for the two-source model are shown in Table 3.

TABLE 2. Shop 2: Source Fingerprints (wt%)

	Source	
Fitting Element	**Conversion Line**	**Continuous Decorative Line**
Si	2.1	3.7
S	26.	9.1
Cl	12.	15.
K	0.0	1.4
Ca	2.9	7.2
Cr	20.	1.9
Fe	2.3	6.4
Ni	1.9	2.2
Cu	0.4	4.0
Zn	18.	23.
Cd	14.	23.
Pb	0.0	2.8

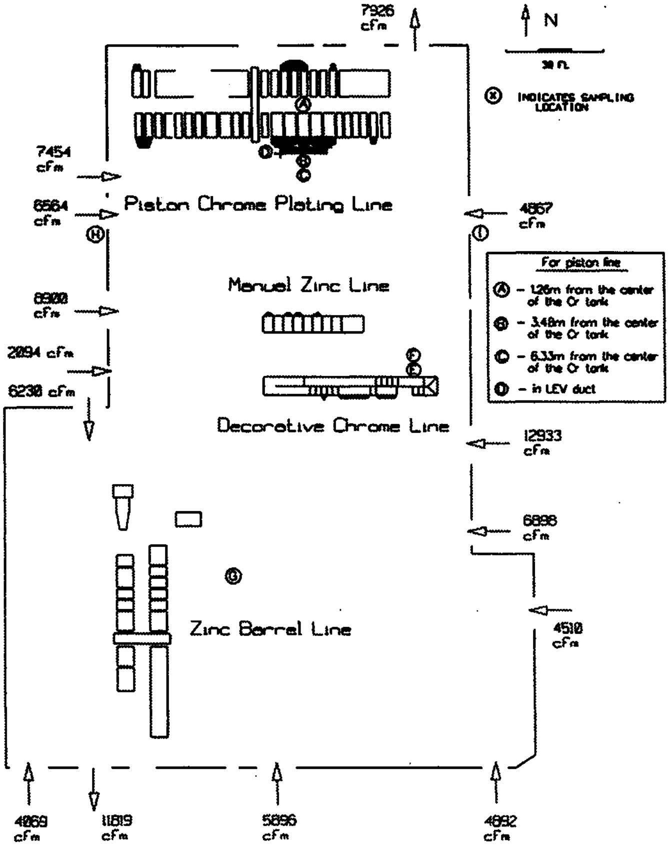

FIGURE 3. Plan view of shop 3 with sampling locations (A, B, C, D, E, F, G, H, and I).

The Three-Source Model. For the three-source model, air entering the room was defined as the third source in addition to the piston and decorative lines. Because the chemical composition for entering air was only measured for 6-hour periods (at locations H and I), the fingerprints of the three-source model were calculated on a 6-hour basis. Two sets of fingerprints were developed. One set was calculated from 6-hour average concentrations which were determined from the measured hourly source concentrations (Table 4). In addition, an attempt was made to determine fingerprints that were more specific to each plating source. Since air from outside the room is a constituent of the measured concentrations in the piston

TABLE 3. Shop 3: Hourly Fingerprints for the Two-Source Model (wt%)

		Hour											
Source	**Element**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Piston line	Cl	3.6	3.2	2.0	2.2	2.4	2.5	8.0	5.8	8.4	6.9	15.	13.
	Cr	82.	87.	87.	90.	89.	91.	53.	62.	51.	66.	56.	50.
	Cu	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.3	0.4	0.6
	Fe	3.7	2.4	2.9	0.9	1.2	1.1	12.	10.	13.	4.9	1.9	6.1
	Ni	0.9	0.9	0.9	1.1	0.9	0.8	1.3	0.9	2.9	2.2	0.6	1.0
	Pb	0.3	0.2	0.2	0.1	0.1	0.1	0.4	0.3	0.2	0.3	0.3	0.7
	S	6.2	3.6	3.9	3.1	3.6	3.3	11.	7.6	8.9	4.9	5.4	12.
	Si	2.4	2.1	2.0	1.9	1.6	0.7	10.	6.4	8.2	5.8	4.3	8.0
	Zn	1.1	0.5	0.7	0.3	0.6	0.5	4.0	6.8	7.0	8.9	16.	9.0
Decorative line	Cl	17.	28.	30.	35.	26.	30.	10.	12.	6.2	17.	38.	14.
	Cr	5.8	3.9	4.2	2.3	3.8	4.0	7.1	2.7	9.8	4.5	3.1	2.5
	Cu	0.9	0.7	0.6	0.4	0.6	0.4	0.4	0.4	0.4	0.3	0.3	0.7
	Fe	16.	18.	15.	14.	12.	15.	21.	30.	19.	14.	10.	15.
	Ni	4.5	5.6	6.1	7.9	7.2	5.1	1.9	2.9	4.5	4.7	5.7	4.6
	Pb	0.7	1.3	1.0	1.2	0.5	0.8	0.6	0.9	0.9	0.9	0.3	0.8
	S	15.	22.	17.	23.	20.	23.	32.	17.	16.	19.	15.	25.
	Si	6.5	13.	5.9	9.4	12.	13.	21.	21.	21.	27.	9.2	29.
	Zn	33.	7.8	21.	6.8	18.	9.2	6.4	14.	22.	12.	18.	8.9

line duct, or near the decorative line, fingerprints were also developed for the two plating lines which excluded the contributions of entering air. A simple CMB model was applied to determine how much the entering air contributed to duct concentrations. The equation is given by

$$Y_{i_{duct}} = \beta_a Z_{a,i} + E_i \qquad (2)$$

where:

$Y_{i_{duct}}$ = the LEV duct fingerprints of the piston line for element i
$Z_{a,i}$ = the outside air fingerprints for element i
β_a = the source coefficient
E_i = the error term for element i

TABLE 4. Shop 3: 6-Hour Average Fingerprints for the Three-Source Model (wt%)

Hour	**Element**	**Piston Line**	**Decorative Line**	**Entering Air**
1 to 6	Cl	2.5	26.	4.5
	Cr	88.	4.6	0.2
	Cu	0.4	0.7	0.6
	Fe	1.8	15.	54.
	Ni	0.9	5.5	1.3
	Pb	0.1	0.8	1.1
	S	3.8	19.	19.
	Si	1.6	8.2	13.0
	Zn	0.6	20.	6.5
7 to 12	Cl	10.	19.	19.
	Cr	56.	4.7	0.8
	Cu	0.4	0.4	0.7
	Fe	7.7	18.	31.
	Ni	1.5	4.0	0.9
	Pb	0.3	0.6	0.4
	S	7.8	21.	16.
	Si	6.7	18.	13.
	Zn	9.6	14.	18.

It was found that all the elements were underpredicted except for iron, which was overpredicted. This suggested that iron concentrations in the LEV duct were due to air coming from outside the room, while in-room sources (e.g., the piston line itself) generated all or much of the other elemental concentrations. Based on this hypothesis, it was assumed that the iron concentrations measured in the duct were all due to out-of-room activities. An adjustment based on iron was made for both 6-hour average duct concentrations on the piston line and the average of E and F concentrations at the decorative line. The adjusted concentrations were calculated by

$$C_{i,adjust} = C_{i,plating} - C_{Fe,plating}(C_i/C_{Fe})_{outside\ air} \qquad (3)$$

where:

$C_{i,plating}$ = the element i concentration in the LEV duct or the average of the (E and F) measurement
$C_{Fe,plating}$ = the iron concentration in the LEV duct or the average of the (E and F) measurement
$(C_i/C_{Fe})_{outside\ air}$ = the concentration ratio of element i to iron in entering air
$C_{i,adjust}$ = the adjusted element i concentration in the LEV duct or in the average of the (E and F) measurement

The $C_{i,adjust}$ values were then normalized by dividing by the sum of the adjusted concentrations for all the fitting compounds. The resulting weight %'s are shown in Table 5. All the

TABLE 5. Shop 3: 6-Hour Average Chromium Plating Line Fingerprints Adjusted to Remove the Contribution of Entering Air (wt%)

Hour	Element	Piston Line	Decorative Line	Entering Air
1 to 6	Cl	2.5	34.	4.5
	Cr	91.	6.3	0.2
	Cu	0.4	0.7	0.6
	Fe	0.0	0.0	54.
	Ni	0.9	7.2	1.3
	Pb	0.1	0.7	1.1
	S	3.2	19.	19.
	Si	1.2	6.4	13.
	Zn	0.4	26.	6.5
7 to 12	Cl	7.0	19.	19.
	Cr	75.	11.	0.8
	Cu	0.3	0.004	0.7
	Fe	0.0	0.0	31.
	Ni	1.6	8.6	0.9
	Pb	0.3	0.9	0.4
	S	5.0	27.0	16.
	Si	4.6	25.	13.
	Zn	6.6	8.2	18.

adjusted 6-hour average concentrations were positive concentrations, which is consistent with the assumption that all iron was contributed from outside air and not from indoor plating processes. Both sets of plating fingerprints were used with the outside air fingerprints in applying the three-source model. (Note: The same type of adjustment to remove the contribution of air outside the room was carried out for the copper plating line fingerprint in shop 1. In this case silicon was used as the reference element. However, the CMB results were essentially the same with or without the adjustment. Consequently, only results using the fingerprints in Table 1 are reported.)

Results

Equation 1 was solved for each area sample at each site for source coefficients representing the contributions of the modeled sources to the total mass of fitting elements. Equation 1, written for one element, represents a mass balance on that component. The source coefficients determined from simultaneously solving all the fitting component mass balances can then be substituted to determine for a particular area sample the amount of element from each source and the amount unexplained. We have presented the results in terms of a particular element of interest: copper for shop 1, and chromium for shops 2 and 3. In Figures 4, 6, 8, and 10, the predicted concentrations from the modeled sources are compared with measured concentrations. Source activities or emission rates were used to check the consistency of the results.

Discussion

Shop 1

CMB RESULTS. All coefficients calculated from the CMB model were positive. This indicates that there was no collinearity problem between the chemical fingerprints for the copper plating line and air from outside the room. The CMB model was able to explain about 100 percent of the copper measured at three locations in the room, 95 to 98 percent of which was determined to come from the plating line. Comparison of predicted and measured copper concentrations is shown in Figure 4 with a coefficient of determination r^2 = 0.96 and a slope of 1.1.

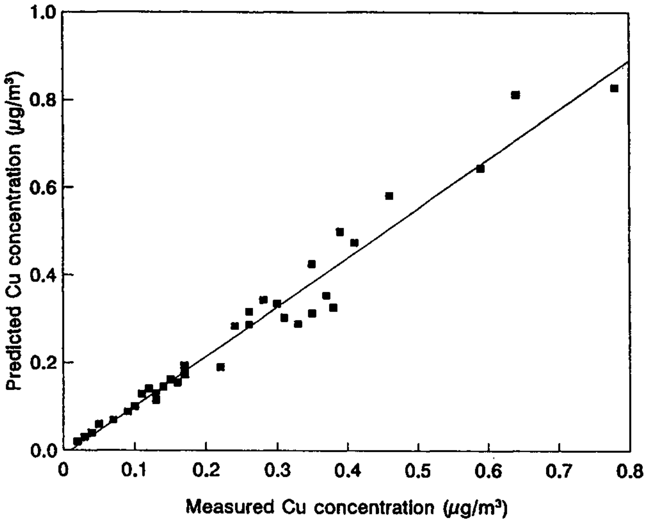

FIGURE 4. Shop 1: predicted versus measured copper concentrations; n = 36, r^2 = 0.96, slope of least-squares fit line = 1.1.

PLATING CONTRIBUTIONS AND ROOM EMISSIONS. The room copper emissions were calculated in a previous study[11] using both an experimental mass balance model and a two-point diffusion model. The relationship of room emissions (determined using the two-point diffusion model) and copper concentrations allocated from plating at location A (Equation 1) are shown in Figure 5. The plot shows a positive association

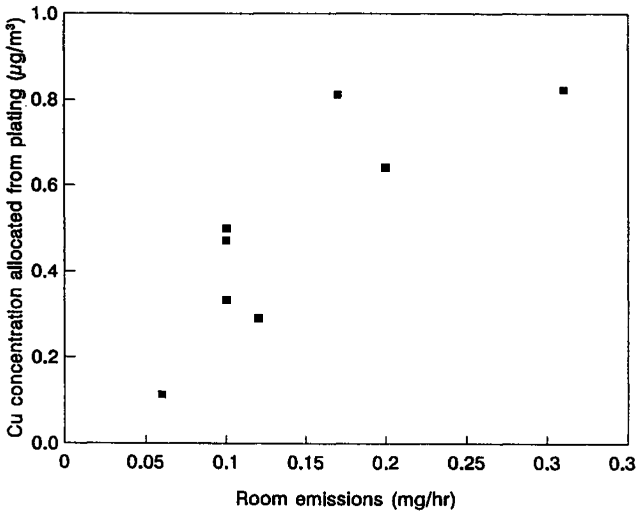

FIGURE 5. Shop 1: copper concentrations at location A allocated from plating versus room emissions from a two-point diffusion model.

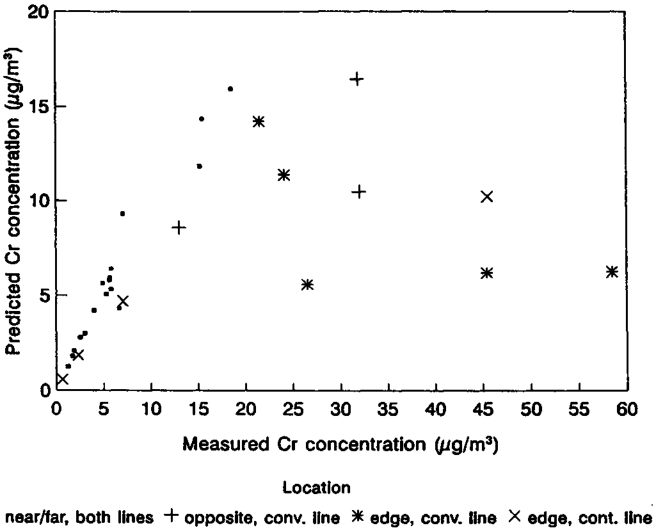

FIGURE 6. Shop 2: predicted versus measured chromium concentrations.

between estimated copper concentrations from the plating line and copper emissions, and the same result was found with experimental mass balance model emissions. This agreement indicates that even though three different mass balance models were used, the results were consistent.

Shop 2

CMB RESULTS. There were only two negative coefficients obtained out of 32 allocations. Consequently, source fingerprint collinearity was not a major calculational problem even though both sources were chromium plating processes (one chemical and one electrochemical). In addition, one of the negative coefficients resulted from allocation of the edge sample of run 1 at the conversion line. The original article reporting these data[(12)] noted that this sample was suspected to have been contaminated by splashing from the tank solution. The chromium concentration was 522 $\mu g/m^3$, which was much higher than the rest of the observations.

Based on all the area samples, the two plating lines contributed an average of 78 percent of the measured chromium concentrations, with 62 percent from the conversion line and 16 percent from the continuous line. The results were qualitatively consistent with the previous study:[(12)] the collection efficiency for the LEV system of the conversion line was much lower than that of the continuous line.

Figure 6 shows a comparison of predicted versus measured concentrations. At five sampling locations [the near and far locations of both lines, and except for one value, the edge location of the continuous line (Figure 2)], the model allocated essentially 100 percent of the measured chromium concentrations to the two chrome plating lines. Chromium concentrations were underpredicted for the opposite and edge locations of the conversion line. This underprediction was the reason that, based on all the samples, on average 22 percent of the chromium remained unallocated after the contributions from the two plating lines had been accounted for.

In an attempt to understand the lack of agreement for the opposite and edge conversion line positions, we examined the other activities that were occurring during the test. The elevated residual chromium concentrations at the two sampling sites suggested that other sources of chromium, not identified during the test, were contributing at these two sites, causing the underestimation. The manual electroplating lines were intermittently operated during sampling periods. No concentration data were available, but activities for the manual lines were recorded during the test. To test whether manual line activity may have contributed to chromium concentrations, the chromium residuals and activities at manual lines were compared.

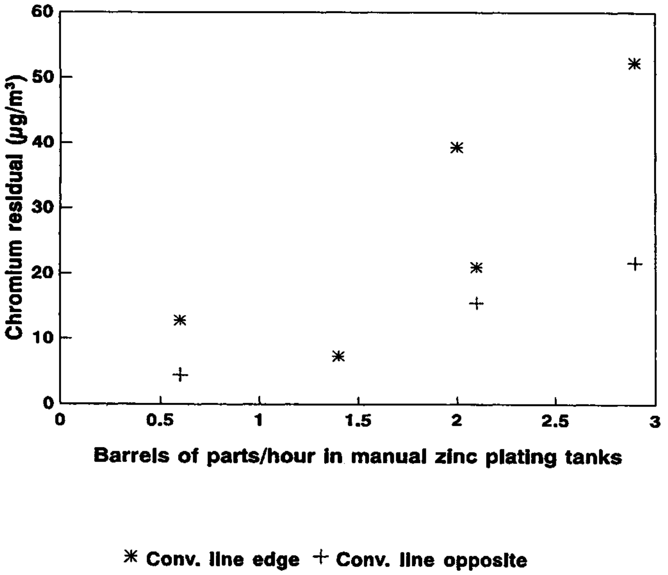

FIGURE 7. Chromium residual concentrations for the two locations nearest the manual zinc plating line versus zinc line throughput.

CHROMIUM RESIDUALS AND MANUAL LINE ACTIVITIES. Chromium residuals, the differences between the predicted and measured concentrations, can be interpreted as experimental error and/or as the contributions from sources not included in the model. Because no samples were collected around the manual electroplating lines and no specific observations of barrels entering the chromium tanks were recorded, the activities of the zinc tanks[(15)] were used to compare with the chromium residuals. The actual sequence of plating was not recorded for the manual lines, but it is likely that barrels of parts in the zinc baths also had been immersed in the chromium tanks at some point in the plating cycle.

Figure 7 shows a positive association between the chromium residuals from both conversion line locations and the number of barrels of parts rotating in the zinc tanks. The scatter of the data should be expected. Workroom emissions are a function of many variables. Consequently, number of barrels of parts is only an approximate measure of chromium release, and the association need not be linear. Chromium residuals at the opposite site, closest to the manual line (Figure 2) and situated so that splashing was not a problem, were closely related to manual line activity. The edge location may have been more susceptible to the effect of splashing, and hence the greater scatter of the data. Given these limitations, the apparent rela-

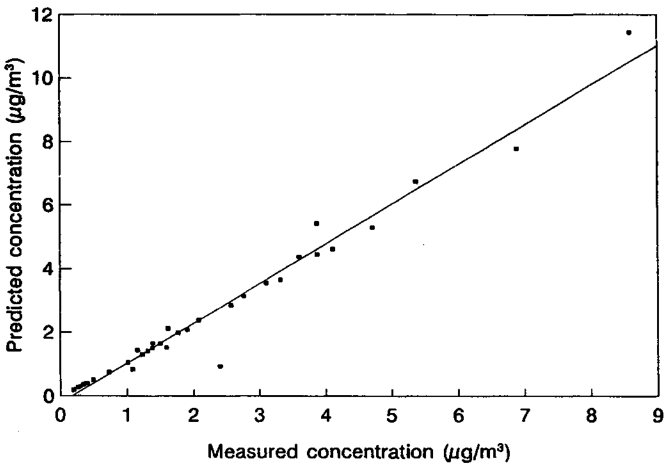

FIGURE 8. Shop 3: predicted versus measured hourly chromium concentrations for the two-source model based on hourly fingerprints; n = 38, r^2 = 0.97, slope of least-squares fit line = 1.25.

tionship displayed in Figure 7 between a crude measure of release and residual chromium is strong evidence that the manual plating line was an additional source.

This analysis also demonstrates that evaluation of residual concentrations for each fitting compound may be able to provide additional information about other workroom activities not originally identified as sources. We didn't discover the manual line contribution until the data were plotted (the field test was not designed as a CMB receptor model when it was carried out(12)), but the data showed that the manual line was a possible source in addition to the two automated lines. The strength of the model is that it identifies an unrecognized source (i.e., by a large, positive residual of one or more fitting compounds) even though the sources were not identified in the field.

Shop 3

TWO-SOURCE MODEL.

CMB Results. Forty-four pairs of source coefficients were calculated from the two-source CMB model using hourly unadjusted fingerprints and hourly area concentrations at locations A, B, C, and G. Only six samples resulted in negative coefficients: two at location C and four at location G. Samples at location G were taken as a room background away from the electroplating lines (Figure 3). It was reasonable that the CMB model did not predict as well for location G because it was much farther away from the modeled sources, and four chromium concentration measurements were less than the detection limit at this location.

A strong association between predicted and measured concentrations is presented in Figure 8 with a coefficient of determination of 0.97 and a slope of 1.25. The CMB model was able to explain about 100 percent of the hourly average chromium measured at four locations in the room (108, 113, 103, and 110% for locations A, B, C, and G). For the three locations in the vicinity of the piston line, the average estimated chromium concentrations from the piston line decreased with distance away from the line, with contributions of 92 percent for location A, 87 percent for location B, and 59 percent for location C (Table 6). For the decorative line, the chromium contributions also decreased with distance, with 8 percent for location A, 13 percent for location B, and 41 percent for location C (the closest to the decorative line).

TABLE 6. Shop 3: Average Two-Source CMB Allocations of Chromium Using Hourly Fingerprints

	Average Contribution (µg/m³)			Average % Contribution	
Location	**Piston Line**	**Decorative Line**	**Measured**	**Piston Line**	**Decorative Line**
A (closest to piston line)	3.5	0.17	3.2	92	8
B (between A and C)	2.7	0.26	2.5	87	13
C (closest to decorative line)	0.70	0.21	0.86	59	41

Chromium Contributions and Room Emissions. The hourly chromium emissions determined in a previous study(13) are compared in Figure 9 with allocated piston line concentrations at sample location B. There is a positive association between emissions and CMB estimates. We did not have an estimate of emissions for the decorative line and therefore could not carry out the same comparison.

THREE-SOURCE MODEL.

CMB Results. Six-hour predicted chromium concentrations agreed well with average measured values, regardless of which set of fingerprints was used. Figure 10 shows the association using the fingerprints, with the effect of air removed (Table 5).

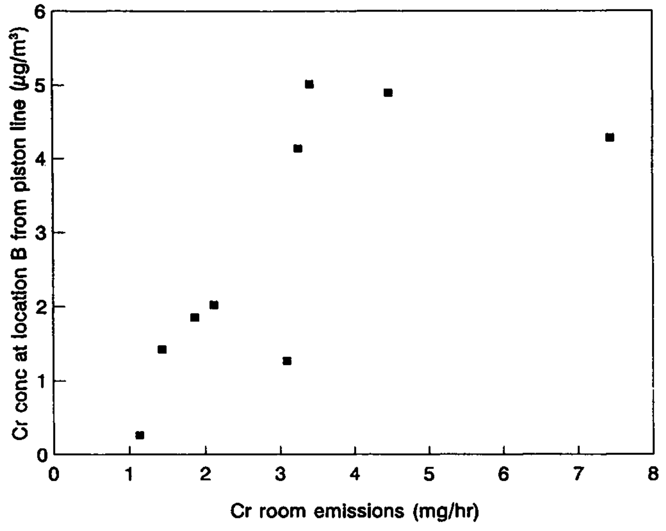

FIGURE 9. Shop 3: hourly chromium concentrations allocated from the piston line at location B versus piston line chromium room emissions.

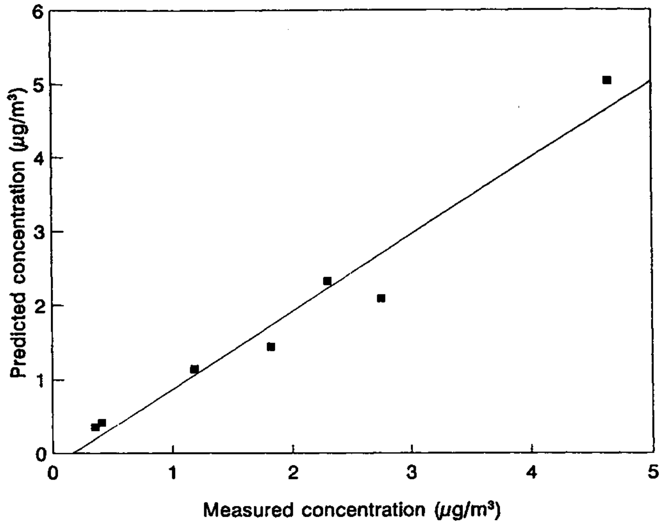

FIGURE 10. Shop 3: predicted versus measured chromium concentrations for the three-source model based on adjusted 6-hour average fingerprints; n = 7, r^2 = 0.95, slope of least-squares fit line = 1.0.

Chromium Contributions and Energy Used on a 6-Hour Basis. Energy expended in electroplating is sometimes used as a very approximate surrogate for emissions.$^{(13)}$ Figures 11 and 12 show chromium allocations from each line plotted versus the ampere • hours/hour for the respective line. This evaluation was based on the plating fingerprints with the effect of air removed and the three-source model. Although the comparison is limited to two points, the results from both lines are consistent with the measures of energy use on each line. It should also be noted that the plots for the piston line and the decorative line are on different scales.

Conclusions

We have presented the modeling results in terms of particular elements of interest, in this case chromium and copper. However, all fitting elements enter into the calculation, and a mass balance on each of the elements is a result of the CMB allocation. Consequently, for every area sample an allocation from each source is made for each fitting compound. As an example, for shop 2 the fingerprints for cadmium were 13.7 percent for the conversion line and 23.4 percent for the continuous line. Based on application of the CMB to each of 30 area samples, the mean contribution of each identified source, the residual value, and the mean measured cadmium concentration are shown in Table 7. About 91 percent of the cadmium is explained by the two plating processes.

Table 7 summarizes the average predicted contribution from each identified source for each shop. We have also included

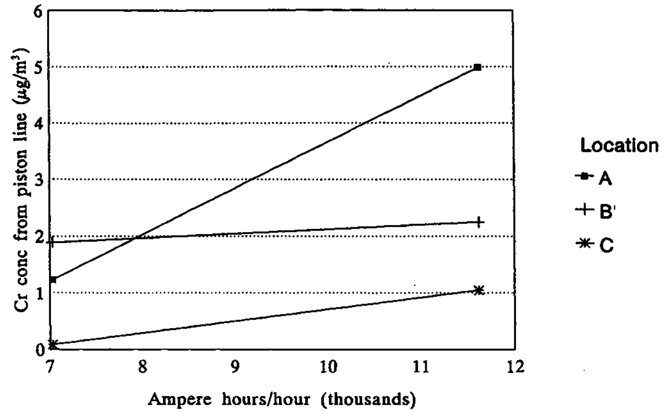

FIGURE 11. Shop 3: chromium concentrations at locations A, B, and C allocated from the piston line versus ampere•hours/hour used by the line (three-source model based on adjusted 6-hour fingerprints).

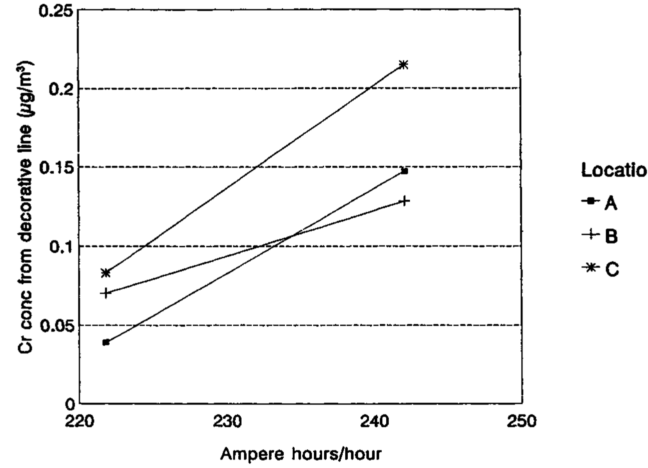

FIGURE 12. Shop 3: chromium concentrations at locations A, B, and C allocated from the decorative line versus ampere•hours/hour used by the line (three-source model based on adjusted 6-hour fingerprints).

TABLE 7. Comparison of Average Measured Concentrations with Allocated Values for Selected Fitting Elements

	Cu (µg/m³)	S (µg/m³)	Ni (µg/m³)
Shop 1, n = 36			
Copper plating line	0.26	0.57	0.003
Entering air	0.01	0.87	0.0002
Measured	0.25	2.29	0.005

	Cr (µg/m³)	S (µg/m³)	Ni (µg/m³)	Cd (µg/m³)
Shop 2, n = 30				
Conversion line	6.2	8.0	0.58	4.2
Continuous line	0.7	3.2	0.79	8.4
Measured	14.2	11.9	4.8	13.8

	Cr, (µg/m³) (n = 38)	S (µg/m³) (n = 39)	Ni (µg/m³) (n = 42)
Shop 3			
Piston line	1.7	0.14	0.03
Decorative line	0.2	0.77	0.20
Measured	1.7	2.6	4.3

the average measured values for each element of interest. It should be noted that none of the data sets were collected with the intention of applying the CMB model. The application was carried out later to see if additional quantitative information could be recovered about process emissions. Consequently, other sources not included in our regression models may have been operating but were unrecognized during our tests. However, analysis of the residual concentrations often provided a clue to the presence of additional sources. This is evident for sulfur in shop 1, nickel and chromium in shop 2, and sulfur and nickel in shop 3. (We observed open nickel plating tanks in shops 2 and 3 but had no chemical data to further describe the operations.)

The CMB model appears to be a useful method for allocating specific source contributions to area concentration measurements in spaces containing multiple sources. Very few negative source coefficients were determined from the CMB model calculations, which suggests that there was no collinearity problem in the fingerprints of the modeled sources. Good agreement was found between CMB-predicted concentrations of copper or chromium and measured concentrations. When there was disagreement, it was often possible to identify sources not included in the model which contributed to the measured concentrations.

The method, as we have applied it, requires speciation of particulate samples, although not necessarily by PIXE analysis. The *OSHA Technical Manual*(17) indicates that 12 metals, many of which were included in our fingerprints, can be determined for a single sample by inductively coupled plasma analysis. The cost of analyzing a sample for all 12 elements is presently about $75.00, versus $25.00/element by atomic absorption. So for a modest increase in price, the investigator can gain considerably more information about the process and the requirements for controls.

It is also necessary to collect multiple samples in order to measure the variability in the source emissions. In general we have found that a 1-hour averaging time is most convenient. Our usual test protocol calls for 12 1-hour samples collected at each sampling location distributed over two shifts. For research purposes we monitor at as many locations as we can afford or service. The practitioner may have more constraints. However, at the minimum, hourly samples should be collected at each recognized source and at several area sampling points. The procedure is useful to apply both before controls are implemented, to determine which sources should be restricted and how much, and after installation, to determine the control effectiveness.

The same approach can also be used to allocate specific source contributions to personal exposures when a space contains two or more sources of a pollutant. For example, in the case of shop 3, typically 90 percent of the measured chromium concentrations at the locations nearest to the piston line (A and B) was contributed from the hexavalent chromium plating line (the piston line). Since the sample analysis method did not discriminate the chromium oxidation state, the CMB allocation provided a first-cut method for estimating how much of the exposure at these locations was in the more toxic hexavalent form.

Acknowledgments

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