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APPLICATION OF CHEMICAL MASS BALANCE MODELING TO INDOOR VOCs

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ABSTRACT

There have been several studies to measure the concentrations of volatile organic compounds (VOCs) indoors and to characterize their sources. However, the two tasks have often been done separately, and few attempts have been made to provide a direct link between the sources and the measured VOCs. Chemical mass balance (CMB) modeling was applied to the measurements of 24 VOCs in a newly constructed house. The results of CMB modeling show that wall adhesive, caulking, I-beam joist, and particleboard are the dominant sources. An attempt was also made to estimate the source contributions using mathematical transport modeling. Good agreement was obtained between the two results. The CMB model is shown to have good potential for identifying the dominant sources and helping develop control strategies for indoor VOCs. However, more research is needed for the collinearity problem associated with source signatures.

INDEX TERMS

Source apportionment, Chemical mass balance, VOCs, Indoor air, Building materials

INTRODUCTION

The chemical mass balance (CMB) model, a source apportionment technique, has been widely used in outdoor air pollution studies to identify emission sources responsible for the measured concentrations of particulates and VOCs (Henry *et al.*, 1984; Waston, Chow, and Fujita, 2001). This information has been found to be useful in developing pollution control strategies. However, there have been few attempts to apply the CMB model to indoor air quality studies to link emission sources with measured VOCs in the air.

Source apportionment techniques attempt to identify the contributions of sources responsible for the chemical compounds identified at a sampling site based on the measured concentrations. These techniques are also referred to as receptor modeling. On the other hand, mathematical transport modeling, which has been frequently used in indoor air quality studies, estimates the contributions of emission sources to the chemical concentrations in the air based on fundamentals of chemistry and physics (Seinfeld and Pandis, 1997). Since receptor modeling considers the transport mechanism between sources and receptors as a black box, it needs little or no prior information on sources and transport processes. The objective of this study is to show the applicability of CMB modeling to indoor air quality studies by identifying dominant indoor sources based on the measured VOC concentrations in the air.

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METHODS

Chemical mass balance model

The concentration of a pollutant at a sampling location can be considered as the summation of the contributions from various sources:

$$x_i = \sum_j^p a_{ij} s_j \quad i = 1, \dots, m \quad (1)$$

where x_i is the predicted concentration of pollutant i at a sampling location,
 a_{ij} is the source signature for pollutant i from source j , which will be obtained from a material emissions database developed by Institute for Research in Construction,
 s_j is the contribution of source j , which is the unknown and to be solved,
 m is the number of pollutants, and
 p is the number of sources.

The value of s_j can be found by minimising the difference between the measured (C_i) and the predicted (x_i) concentrations:

$$\xi^2 = \sum_i^m \left[\frac{1}{\sigma_i^2} (C_i - \sum_j^p a_{ij} s_j)^2 \right] \quad (2)$$

This is the common multiple regression analysis problem (Seinfeld and Pandis, 1997). When the uncertainties (σ_i) in the measurements are assumed to be constant among pollutants, the solution method is referred to as least squares. The least squares solution of Eq. 2 is the vector \mathbf{s} of source contributions given by Eq. 3.

$$\mathbf{s} = [\mathbf{A}^T \mathbf{A}]^{-1} \mathbf{A}^T \mathbf{c} \quad (3)$$

where \mathbf{A} is the $m \times p$ source signature matrix with the source composition a_{ij} ,
 \mathbf{A}^T is the transpose matrix of \mathbf{A} ,
 \mathbf{c} is the vector with the concentration measurements.

The solution vector \mathbf{s} was obtained for 20 sets of VOC measurements and was averaged later.

Application to VOC field measurements

VOC concentration measurements were obtained during and after the construction of the "Reference" house, which is one of two research houses under the project of the Canadian Center for Housing Technology (CCHT). Air samples in the house were collected on Carbotrap 300 sorbent tubes followed by thermal desorption and GC/MS analysis. The quantification for each VOC was based on the response curve of toluene. A total of twenty samples were collected between 127 and 311 days after the foundation of the house was poured.

Since the house was newly constructed and unoccupied, only building materials were considered as sources. The average source signatures were obtained for materials in the same category from the material emissions database developed by Institute for Research in Construction. This type of general source signatures is useful, considering that source signatures for specific materials of interest in most test houses are unlikely to be readily available.

Table 1. Source signature (a_{ij}) for 24 VOCs from 10 building materials

VOCs	Concentration/Sum of concentrations of 24 VOCs									
	WS ^a	GB ^a	OSB ^a	CRP ^a	WV ^a	IBJ ^a	CK ^a	PLY ^a	PB ^a	AD ^a
Benzene, 1-ethyl-3-methyl-	-	0.007	-	-	-	-	0.034	-	-	0.023
Benzene, 1,2,3-trimethyl-	-	0.009	-	-	-	-	0.037	-	-	0.041
Benzene, 1,2,4-trimethyl-	-	0.021	-	-	-	-	0.049	-	-	0.045
Camphene	-	0.002	-	-	-	0.075	-	0.048	0.172	-
3-Carene	-	-	-	-	-	-	-	0.141	0.064	-
Cyclohexane, butyl-	0.069	-	-	-	0.026	-	0.037	-	-	0.036
Cyclohexane, 1,1,2,3-tetramethyl	0.058	-	-	-	-	-	0.043	-	-	0.011
Cyclohexane, propyl-	0.058	-	-	-	-	-	0.040	-	-	0.017
Decane	0.203	0.069	-	0.065	0.288	-	0.265	0.052	-	0.265
Decane, 3-methyl	0.048	0.010	-	-	0.061	-	0.033	-	-	0.027
Decane, 4-methyl	0.039	0.012	-	-	-	-	0.023	-	-	0.035
Dodecane	0.065	0.017	-	0.103	0.022	-	0.027	-	-	0.041
Hexanal	-	0.009	0.918	-	-	0.004	-	0.084	0.054	-
Limonene	-	0.003	-	0.041	-	0.064	0.006	0.263	0.145	-
Nonane	0.136	0.010	-	-	0.154	-	0.104	0.031	-	0.082
Nonane, 2-methyl-	0.060	0.005	-	-	0.034	-	0.046	-	-	0.025
Nonane, 3-methyl-	0.093	0.005	-	-	0.040	-	0.054	-	-	0.029
Nonane, 4-methyl-	0.060	0.007	-	-	0.030	-	0.055	-	-	0.030
α -Pinene	-	0.011	0.041	-	-	0.713	-	0.251	0.500	-
β -Pinene	-	0.727	-	-	-	0.144	-	0.112	0.065	-
Toluene	-	-	0.010	0.033	-	-	0.010	0.007	-	-
Undecane	0.109	0.074	0.031	0.108	0.346	-	0.127	0.010	-	0.278
Undecane, 2-methyl-	-	-	-	-	-	-	0.010	-	-	-
<i>p</i> -Xylene	-	-	-	0.650	-	-	-	-	-	0.013
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

^a WS: wood stain (2), GB: gypsum board (3), OSB: oriented strand board (4), CRP: carpet (6), WV: wood varnish (1), IBJ: I-beam (1), CK: caulking (2), PLY: plywood (4), PB: particleboard (3), AD: wall adhesive (1). The value in parenthesis is the number of materials used for averaging.

RESULTS

Source contributions by CMB modeling

The results of CMB modeling are listed in Table 2. The negative values of source contributions in the second column are most likely due to the similarities in source signatures. The collinearity problem is not uncommon in CMB and can result in large uncertainties as well as negative values for estimated source contributions (Henry *et al.*, 1984).

Table 2. Source contribution (s_i) from CMB modeling

	CMB	CMB w/ grouping
Wood stain	0.847	0.021
Gypsum board	-0.069	0.013
Oriented strand board	0.010	0.004
Carpet	-0.001	0.052
Wood varnish	-0.743	0.178
Plywood	0.585	0.176
I-beam joist	0.882	0.889
Particleboard	-0.352	
Wall adhesive	2.691	1.945
Caulking	-0.569	

It is suggested that each near linear dependence among the vectors of the source signature matrix \mathbf{A} will manifest itself in a small singular value, which is the square root of eigenvalue of $\mathbf{A}^T \mathbf{A}$ (Belsely *et al.*, 1980). Therefore, condition number (μ), i.e., the ratio of the maximum

singular value to a singular value of **A**, can be adopted as a measure of collinearity. Belsely *et al.* (1980) employed the condition index threshold of 10 for weak dependencies. The analysis for variance-decomposition proportions can be another measure of collinearity. The estimated variance of each regression coefficient may be decomposed into a sum of terms each of which is associated with a singular value, thereby providing means for determining the extent to which near dependencies degrade each variance. Consequently, the dependent source signatures can be identified by the joint occurrence of high variance-decomposition proportions for two or more coefficients associated with a single singular value having a "high" condition index (Belsley *et al.*, 1980).

Systat 10 was used to calculate variance-decomposition proportions and condition indexes for the source signature matrix **A** (Table 3). The condition index of 21 suggests that there are weak or moderate dependencies among some source signatures. The value of 0.7 was employed as the cut-off for the high value of variance-decomposition proportions to identify sources of collinearity. The 9th singular value accounts for 70% or more of Var(s₇) and Var(s₁₀), which indicates that source signatures of caulking and wall adhesive are similar enough to cause collinearity. Additionally, the 10th singular value accounts for 80% or more of Var(s₆) and Var(s₉), which also suggests that I-beam joist and particleboard have similar source signatures.

Table 3. Variance-decomposition proportions and condition index of source signature matrix

Singular value	Var(s ₁) for WS	Var(s ₂) for GB	Var(s ₃) for OSB	Var(s ₄) for CRP	Var(s ₅) for WV	Var(s ₆) for IBJ	Var(s ₇) for CK	Var(s ₈) for PLY	Var(s ₉) for PB	Var(s ₁₀) for AD	Condition index
μ_1	0.000	0.027	0.149	0.001	0.000	0.012	0.000	0.004	0.003	0.000	1
μ_2	0.000	0.018	0.749	0.000	0.000	0.005	0.000	0.000	0.001	0.000	1
μ_3	0.002	0.062	0.000	0.096	0.004	0.002	0.001	0.000	0.000	0.001	1
μ_4	0.000	0.534	0.004	0.163	0.000	0.002	0.000	0.000	0.001	0.000	1
μ_5	0.001	0.067	0.001	0.659	0.003	0.000	0.001	0.000	0.000	0.001	2
μ_6	0.000	0.014	0.082	0.001	0.001	0.116	0.000	0.349	0.003	0.000	4
μ_7	0.152	0.001	0.003	0.007	0.082	0.003	0.034	0.003	0.001	0.011	6
μ_8	0.296	0.001	0.000	0.004	0.242	0.000	0.188	0.000	0.000	0.114	10
μ_9	0.543	0.016	0.001	0.069	0.664	0.012	0.776	0.053	0.026	0.871	21
μ_{10}	0.005	0.262	0.011	0.000	0.003	0.846	0.000	0.590	0.965	0.002	11

Hopke *et al.* (1984) suggests that grouping similar sources may provide a solution, although the resolution of the source apportionment is compromised. Based on the results of Table 3, caulking and wall adhesive were grouped into one source with the averaged source signature. The maximum value of condition index was lowered to 13, but some of source contributions remained negative. Additional grouping for I-beam joist and particleboard lowered the maximum value of condition index to 12 and provided non-negative source contributions (Table 2). The R² value for CMB modeling with 8 sources was 0.82, which is greater than the threshold of 0.8 suggested in Waston, Chow, and Pace (1991).

Comparison to source contributions by mathematical simulation modeling

The source contributions obtained from CMB modelling were compared to those estimated from a single zone mathematical simulation (SMS) model. Simulation was conducted for each of the 10 sources (materials) individually. The source contributions by the SMS model were determined on the percentage basis by normalizing the concentration from each source by the total concentrations from all sources. Table 4 provides input data for the SMS model, including emission models for total VOC, area of sources, and input time of each source into

the house. For dry materials, the power law decay model was used (Eq. 4). Three different models used for wet materials: the evaporation controlled model (Eq. 5) for $0 < t < t_1$, the exponential decay model (Eq. 6) for $t_1 < t < t_2$, and the power law decay model (Eq. 4) for $t > t_2$.

$$E = a t^{-b} \quad (4)$$

$$E = K_m \left[\left(C_v \frac{M(t)}{M_{01}} - C(t) \right) \right] \quad (0 < t < t_1) \quad (5)$$

$$E = E(t_1) e^{-k(t-t_1)} \quad (t_1 < t < t_2) \quad (6)$$

where a and b are empirical constants, t is the elapsed time (h),
 K_m is the convective mass transfer coefficient ($\text{m}^2 \text{h}^{-1}$),
 C_v is the initial surface concentration (mg m^{-3}),
 M_{01} is the initial mass available for evaporation (mg m^{-3}),
 $E(t_1)$ is the emission factor at $t = t_1$,
 k is the emission decay constant,
 t_1 is the time at which the transition period began (h),
 t_2 is the time at which the diffusion controlled period began (h).

The volume of the house is 794.3 m^3 and the air change rate is 50 h^{-1} (0 - 106 days), 0.25 h^{-1} (107 - 155 days), and 0.23 h^{-1} (156 - 311 days).

Table 4. Input data for the single-zone mathematical model

	Area (m^2)	In Time (d)	t_1 (h)	M_{01} (mg m^{-2})	K_m (m h^{-1})	C_v (mg m^{-3})	t_2 (h)	$E(t_1)$ ($\text{mg m}^{-2} \text{h}^{-1}$)	k (h^{-1})	a	b
WS ^a	5	102	7	40237.42	1.13	39111	24	294.72	0.11811	16024	1.8891
GB	283.2	101	-	-	-	-	-	-	-	31.979	1.063
	283.2	102	-	-	-	-	-	-	-	31.979	1.063
OSB	34.8	9	-	-	-	-	-	-	-	1.509	0.3201
	34.8	10	-	-	-	-	-	-	-	1.509	0.3201
	5.56	168	-	-	-	-	-	-	-	1.509	0.3201
CRP	63.5	116	-	-	-	-	-	-	-	7.414	0.8421
	63.5	119	-	-	-	-	-	-	-	7.414	0.8421
WV	5	123	7	78676.46	1.13	62556	24	915.17	0.1618	2875.5	1.2261
IBJ	28.7	9	-	-	-	-	-	-	-	64.818	0.6264
	28.7	10	-	-	-	-	-	-	-	64.818	0.6264
CK	0.1	76	4	199366	1.13	78055	24	15078	0.022997	59810	0.5783
PLY	5.56	105	-	-	-	-	-	-	-	57.39	1.4222
PB	1.5	30	-	-	-	-	-	-	-	25.108	0.395
AD	0.1	105	2	13229.94	1.13	2056.4	24	1615	0.00368	31512	0.9602

^a WS: wood stain, GB: gypsum board, OSB: oriented strand board, CRP: carpet, WV: wood varnish, IBJ: I-beam joist, CK: caulking, PLY: plywood, PB: particleboard, AD: wall adhesive.

The relative source contributions (%) by the CMB model with grouping and the SMS model are compared in Table 5. The group of caulking and wall adhesive is shown to be the most dominant source with 59% contribution by both models. The second dominant source group is predicted to be I-beam joist and particleboard by two models, although the magnitude of the contribution is different each other. The four sources, i.e., caulking, wall adhesive, I-beam joist, and particleboard, appear to account for 86% (CMB) and 77% (SMS) of VOCs in the house. The next dominant sources are identified to be wood varnish and plywood by the CMB model, while they are gypsum board, wood varnish, and oriented strand board by the SM model. Wood stain and carpet are predicted to be insignificant sources by both models. The agreement in source contributions between the CMB and SMS model is concluded to be

very good, considering the fact that source signatures for the CMB model are the averages of several materials in the same category and the source model for the SM model is based on one material.

Table 5. Source contribution (s_i) in percentage by the CMB and SMS model

	<i>CMB w/ grouping</i>	<i>SM</i>
Wood stain	1	0
Gypsum board	0	7
Oriented strand board	0	6
Carpet	2	3
Wood varnish	5	6
Plywood	5	0
I-beam joist	27	18
Particleboard		
Wall adhesive	59	59
Caulking		
<i>Sum</i>	<i>100</i>	<i>100</i>

CONCLUSION AND IMPLICATIONS

Chemical mass balance modelling was applied to identify the dominant sources of VOCs in indoor air in a newly constructed house. Chemical mass balance modeling identified four dominant sources including caulking, wall adhesive, I-beam joist, and particleboard. The results agree well with those by single zone mathematical simulation modeling. This shows that chemical mass balance modeling has a potential in identifying the most influential sources of VOCs in indoor air based on the VOC measurements and published dynamic emission test results on individual materials. However, it was shown that similar source signatures could cause collinearity, which can result in unrealistic source contributions. Therefore, more research on handling the collinear problem is needed for more general application of chemical mass balance modeling to VOCs indoors.

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