Improvement of receptor model use in analytical aspect

Chu-Fang Wang^a, Pen-Chi Chiang^b, Man-Ting Cheng^c, Hung-Lung Chiang^{d,*}

^aDepartment of Biomedical Engineering and Environmental Science, National Tsing-Hwa University, Hsinchu 30013, Taiwan

^bGraduate Institute of Environmental Engineering, National Taiwan University, Taipei 10617, Taiwan

^cDepartment of Environmental Engineering, National Chung-Hsing University, Taichung 402, Taiwan

^dDepartment of Health Risk Management, China Medical University, Taichung 40402, Taiwan

Received 10 April 2007; received in revised form 24 July 2007; accepted 30 July 2007

Abstract

In this study, four certified particle standards including NIST SRM 1648 urban particulate matter, BCR Reference Material No. 176 city waste incineration ash, NIST SRM 2709 San Joaquin soil, and NIST SRM 1633b coal fly ash were used to simulate ambient particulate matter. Twenty-five samples were prepared with the four certified particulate standards. A total of 23 elements were analyzed per sample, 19 by ICP-AES and ICP-MS, three by IC, and one element, Si, by spectrophotometer. Results showed that combining the three IC-analyzed ionic species with the 19 ICP-AES/MS analyzed elements into the CMB model did not improve the source identification significantly. In addition, when all 23 analyzed chemical species per sample were used in the CMB model, they were still not good enough to effectively make the parameters of the CMB model fit the statistical criteria. Some of high variation and low recovery chemical species, i.e. Cd, V, Sb, etc., may have caused poor CMB model simulation. Omitting some poor quality analyzed species (such as relative analysis error >20%) could improve the CMB model simulation. Therefore, high quality chemical species data are important for the CMB model. In addition, co-linearity of source profiles also affects the CMB model; combining the co-linear sources could enhance the solubility of the CMB model. In this study, a two-step procedure was developed for CMB model simulation to improve source identification.

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Keywords: Chemical mass balance (CMB); Receptor model; Fingerprints

1. Introduction

Since it was first proposed in the early 1970s (Hidy and Friedlander, 1972; Kneip et al., 1972; Winchester and Nifong, 1971), the chemical mass balance (CMB) receptor model has become one of the most successful mathematical methods used to apportion potential source contributions and to

develop appropriate air quality management strategies (Gordon, 1980, 1988; Hopke and Dattner, 1982, 1985; Watson, 1989; Begum et al., 2005; Kim et al., 2005; Marmur et al., 2005; Ward and Smith, 2005; Feng et al., 2006). However, one of the largest impediments to the receptor model today is the lack of accurate, precise, and comparable analytical data for determining chemical profiles (“fingerprints”) of ambient and source data sets (Wang et al., 1995a, b; Robinson et al., 2006; Bhawe et al., 2007).

The chemical composition of ambient air samples is by no means needed quantitatively as input for

*Corresponding author. Tel.: +886 4 2207 9685;
fax: +886 4 2207 9687.

E-mail address: hchiang@mail.cmu.edu.tw (H.-L. Chiang).

the CMB receptor model. The obtained analytical data contain not only direct information on the concentrations measured during each sampling period, but also a wealth of indirect information in the correlations that exist between the pollution sources and sampling sites (Gordon, 1980). The CMB model input data include the ambient concentrations of various species and their fractional amount in each source-type emission. However, even with the best of sampling and analytical methods, only a limited number of species are generally available for the subsequent model analysis. Thus, in a complex air shed, the resolution and precision of the model analysis may not only be limited by the number of chemical species but also by the reliability of these data on which the mathematical analysis is based. To obtain a better CMB result the uncertainty estimates of these values are required. It is therefore necessary to weigh the importance of input data values in the solution and to calculate the uncertainties of the source contributions. Currently used CMB software (Watson et al., 1990, 1998; Christensen, 2004; Christensen and Gunst, 2004) applies the effective variance solution which can provide realistic estimates of the uncertainties for the source contributions and give greater influence to chemical species with higher precision in both the source and receptor measurements than to species with lower precision.

The CMB model assumptions include constant compositions of source emissions, no reaction between chemical species, known characterized information about emission sources, linearly independent of source compositions and enough chemical information about the species. These assumptions for the CMB model are fairly restrictive and difficult to comply with in actual practice. A number of tests to determine the CMB model's abilities to tolerate deviations from these assumptions have been performed (Gordon et al., 1981; Henry, 1982; Currie et al., 1984; Dzubay et al., 1984; DeCesar et al., 1985; Javitz et al., 1988a,b; Christensen and Gunst, 2004). All these tests obtained the same conclusions that deviations from these assumptions increase the stated uncertainties of the source contribution estimates. None of them has ever quantified the influence of accurate and precise chemical information on the estimated source contributions.

This paper evaluates the influence of obtained analytical data on the solution of source contributions via the CMB model analysis and presents a

two-step data evaluation procedure for evaluating the precision of analytical data of CMB modeling instead of optimizing analytical data. To provide sufficient information on air samples in an effort to improve the resolution of receptor model analysis, an experiment using mixed standards to simulate real samples and test the model analysis has been performed.

2. Materials and methods

2.1. Selection of source profiles

To verify the effectiveness of the CMB model from the extent of the number of chemical species and the precision and accuracy of chemical species in samples, four standard sources was selected to simulate the particulate sources in ambient air: (1) NIST SRM 1648 urban particulate matter, (2) BCR Reference Material No. 176 city waste incineration ash, (3) NIST SRM 2709 San Joaquin soil, and (4) NIST SRM 1633b coal fly ash. Among these simulated sources, waste incineration ash and coal fly ash can be categorized as industrial-type "smoke-stacks" and are considered area sources in emission inventories. On the other hand, urban particulate and soil standards represent fugitive emission sources such as wind-blown dust, motor vehicular exhaust, and other emission sources in the metropolitan.

Table 1 lists the certified concentrations of the various species in the selected standard sources which serve as input data for the CMB modeling. For chemical species whose concentration was not certified, a 5% relative standard deviation was estimated. Generally, 5% standard deviation is a criterion for duplicate analysis of standard. Based on the certified species of standard particles, the standard deviation of most species is in the range of 1–10%. When the standard deviation is less than 10%, the effect on the model is insignificant and reasonable (data not shown). A total of 23 species, which can be determined in our laboratory, was used to distinguish one source from another.

2.2. Sample preparation

To effectively study the influence of obtained analytical data on the solution of source contributions via the CMB model analysis, 25 simulated samples (in six groups) were prepared. Table 2 lists

Table 1

Certified concentrations (in ng mg^{-1}) of various chemical species in four different standards

Chemical species	NIST SRM 1648	BCR No. 176	NIST SRM 2709	NIST SRM 1633b
Al	34200 $\pm$ 1100	101000 $\pm$ 5000 ^a	75000 $\pm$ 600	150500 $\pm$ 2700
As	115 $\pm$ 10	93.3 $\pm$ 4.5 ^a	17.7 $\pm$ 0.8	136 $\pm$ 2.6
Ba	737 $\pm$ 37 ^a	3910 $\pm$ 196 ^a	968 $\pm$ 40	709 $\pm$ 27
Ca	5600 $\pm$ 280 ^a	8800 $\pm$ 440 ^a	18900 $\pm$ 500	15100 $\pm$ 600
Cd	75 $\pm$ 7	412 $\pm$ 9	0.38 $\pm$ 0.01	0.784 $\pm$ 0.006
Cr	403 $\pm$ 12	863 $\pm$ 38.0	130 $\pm$ 4	198.2 $\pm$ 4.7
Cu	609 $\pm$ 27	1300 $\pm$ 30	34.6 $\pm$ 0.7	112.8 $\pm$ 2.6
Fe	39100 $\pm$ 1000	21300 $\pm$ 1100	35000 $\pm$ 1100	77800 $\pm$ 2300
K	10500 $\pm$ 100	45000 $\pm$ 2300 ^a	20300 $\pm$ 600	19500 $\pm$ 300
Mg	8000 $\pm$ 400 ^a	21800 $\pm$ 1100 ^a	15100 $\pm$ 500	4820 $\pm$ 80
Mn	786 $\pm$ 17	1390 $\pm$ 70 ^a	538 $\pm$ 17	132 $\pm$ 1.7
Na	4250 $\pm$ 20	43000 $\pm$ 2200 ^a	11600 $\pm$ 300	2010 $\pm$ 30
Ni	82 $\pm$ 3	12.4 $\pm$ 4.2	88 $\pm$ 5	120.6 $\pm$ 1.8
Pb	6550 $\pm$ 80	1090 $\pm$ 17	18.9 $\pm$ 0.5	68.2 $\pm$ 1.1
Sb	4.50 $\pm$ 0.23 ^a	412 $\pm$ 18	0.79 $\pm$ 0.04	6 $\pm$ 0.3 ^a
Si	110000 $\pm$ 5000 ^a	140000 $\pm$ 7000	296600 $\pm$ 2300	230200 $\pm$ 800
Sr	24.4 $\pm$ 1.2 ^a	46.2 $\pm$ 2.3 ^a	231 $\pm$ 2	1041 $\pm$ 14
Ti	4000 $\pm$ 200 ^a	851 $\pm$ 43 ^a	3420 $\pm$ 240	7910 $\pm$ 140
V	127 $\pm$ 7	10.0 $\pm$ 0.5 ^a	112 $\pm$ 5	295.7 $\pm$ 3.6
Zn	4760 $\pm$ 140	25800 $\pm$ 380	106 $\pm$ 3	210 $\pm$ 10.5 ^a
F ⁻	437 $\pm$ 22 ^a	435 $\pm$ 22 ^a	366 $\pm$ 18	405 $\pm$ 20
Cl ⁻	198 $\pm$ 10 ^a	4150 $\pm$ 208 ^a	—	—
SO ₄ ²⁻	154200 $\pm$ 700	9680 $\pm$ 480	70.2 $\pm$ 3.5	475 $\pm$ 24

^aValues are not certified; a 5% relative standard derivation is estimated.

the amount of mass of the various standard sources in each sample.

In group “A”, a 7:1:1:1 ratio of source contribution was designed to investigate the influence of a dominant source on the other minor sources. Group “B” was arranged in a 4:3:2:1 sequential ratio for different standard sources to test whether the apportion order would be altered by the CMB model analysis or not. To determine the capability of the CMB software in distinguishing a non-existent source and colinearity problem, a 1:1:1:0 ratio of source contribution was prepared in group “C” and then tested with all four source profiles in CMB model analysis. Group “D” compared the colinearity occurring between the urban particulate matter source (40% in source profile) and other standard sources (in 4:4:1:1 source profile). Group “E” included three samples with an equal ratio of source contribution but different amounts of mass, which was designed to examine the influence of sample mass on the analytical result as well as model results. Finally, seven randomly prepared samples in various source contributions were tested to verify the effectiveness of the proposed two-step CMB modeling procedure.

2.3. Chemical analysis

During the course of this work, an $\text{HNO}_3 + \text{HClO}_4 + \text{HF}$ (3:5:2 v/v) acid mixture closed vessel digestion method proposed in previous work (Wang et al., 1995a) was employed to completely dissolve the samples. The digested solution was then analyzed by ICP-MS. A Jarrel-Ash ICAP 9000 multi-collector type ICP-AES was employed for determining Al, Ca, Fe, K, Mg, Na, S and Zn while a SCIEX Elan Model 5000 ICP-MS manufactured by Perkin-Elmer was employed for determining As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Sr and V. The detailed experimental procedure can be found in Wang et al. (1996a, b).

For IC analysis, samples were immersed in deionized water and extracted by ultrasonic cleaner (Bransonic) for 4 h. The filtrate was syringed into the Ion Chromatograph (DIONEX, S2000I) for ionic species measurements. Concentrations of Cl^- , F^- , and SO_4^{2-} were then used for receptor model analysis.

Si content was analyzed by spectrophotometer (Himadzu UV-2100) and the method was set up in a previous study (Wang et al., 1997).

Table 2

Masses (mg) and relative ratios of various standard sources in each sample

Sample no.	Mass	SRM 1648	BCR 176	SRM 2709	SRM 1633b
A1	10.0	0.7	0.1	0.1	0.1
A2	10.0	0.1	0.7	0.1	0.1
A3	10.0	0.1	0.1	0.7	0.1
A4	10.0	0.1	0.1	0.1	0.7
B1	10.0	0.4	0.3	0.2	0.1
B2	10.0	0.1	0.4	0.3	0.2
B3	10.0	0.2	0.1	0.4	0.3
B4	10.0	0.3	0.2	0.1	0.4
C1	10.0	0.33	0.33	0.33	0.0
C2	10.0	0.0	0.33	0.33	0.33
C3	10.0	0.33	0.0	0.33	0.33
C4	10.0	0.33	0.33	0.0	0.33
D1	10.0	0.4	0.4	0.1	0.1
D2	10.0	0.4	0.1	0.4	0.1
D3	10.0	0.4	0.1	0.1	0.4
E1	4.0	0.25	0.25	0.25	0.25
E2	8.0	0.25	0.25	0.25	0.25
E3	16.0	0.25	0.25	0.25	0.25
F1	14.1	0.38	0.13	0.18	0.31
F2	12.6	0.34	0.26	0.18	0.21
F3	12.0	0.13	0.41	0.28	0.19
F4	12.9	0.19	0.33	0.23	0.25
F5	13.5	0.27	0.25	0.10	0.38
F6	14.1	0.12	0.13	0.38	0.38
F7	11.6	0.26	0.14	0.34	0.26

2.4. CMB modeling

The CMB model (U.S. EPA standard CMB8.2 software) was used to determine the suspended particulate matter concentration $\mu\text{g m}^{-3}$ contributed to the stations from the potential air pollution sources (EPA, 2000). In order to obtain more accurate and precise estimation results, statistical evaluation with linear least-squares method (LLS) and effective variance techniques (EVT) including percent total mass (PTM, 80–120%), r -square ($r^2 > 0.8$), χ -square statistics ($\chi^2 < 4$) were performed (EPA, 2000).

3. Results and discussion

3.1. Validation of analytical data's quality

During the course of this work, each simulated sample was analyzed at least three times to determine the concentration and variation of each chemical species. The obtained results (M) were compared with the certified values (S), which are

calculated based on the mixed ratios of simulated sources and certified concentrations of various species in each source profile (Tables 1 and 2).

A test of the data's quality is the comparison of measured-to-simulated ratio (M/S) for individual species. Fig. 1 shows the M/S ratios of chemical elements for each sample. For most species, the M/S values lie between 0.9 and 1.1, but several are seriously at variance, notably Cd, As, Ni, V and Sb. The poor fits for these species strongly suggest that there are serious errors in the analytical results of these species.

However, interference problems due to the acid-derived background ions formed during the ion extracting process of ICP-MS can significantly degrade the sensitivities of many elemental determinations, especially that of ^{75}As and ^{51}V (Kawaguchi et al., 1987; Olivares and Houk, 1986). Previous studies (Larsen and Sturup, 1994; Sheppard et al., 1994) revealed that chloride, introduced via reagents or samples, can give rise to the formation of $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{37}\text{Cl}^{14}\text{N}^+$ and $^{35}\text{Cl}^{16}\text{O}^+$, which may seriously inhibit the deviation of $^{75}\text{As}^+$ and $^{51}\text{V}^+$. In addition, the polyatomic interference of $^{25}\text{Mg}^{35}\text{Cl}^-$, and $^{23}\text{Na}^{37}\text{Cl}^-$ could affect the analysis of ^{60}Ni (Hu et al., 2006). Generally, low cadmium recovery is caused by the low Cd content in the sample, spectral interference from other elements i.e. arsenic and iron (Lambkin and Alloway, 2000), and polyatomic ions, i.e., $^{95}\text{Mo}^{16}\text{O}^-$, $^{94}\text{Zr}^{16}\text{OH}^-$, and $^{71}\text{Ga}^{40}\text{Ar}^-$ (Hu et al., 2006).

In addition, the high variation of Mg in samples i.e., B4 and C2 may be attributed to the composed ions (i.e. $^{25}\text{Mg}^{35}\text{Cl}^-$). In addition, the potential was hindered by the presence of molecular interferences (C_2^+ , C_2H^+ , C_2H_2^+ , CN^+ and NaH^+) in the Ar-ICP system (Galy et al., 2001). A major error in Cr determination was due to the Cr loss incurred through volatilization during sample digestion. Many investigators have reported the volatility effect on Cr(VI) from the digestion and evaporation process. Interference problems due to argon gas, filter media, and/or acid-derived background ions, encountered in low-resolution ICP-MS, introduced additional errors in the Cr determination. Specifically, $^{40}\text{Ar}^{12}\text{C}^+$, $^{38}\text{Ar}^{14}\text{N}^+$, $^{35}\text{Cl}^{16}\text{OH}^+$, and $^{35}\text{Cl}^{17}\text{O}^+$ ions inhibit detection of the $^{52}\text{Cr}^+$ isotope. Even for relatively minor isotopes, there is interference (e.g., between $^{53}\text{Cr}^+$ and $^{37}\text{Cl}^{16}\text{O}^+$, and $^{52}\text{Cr}^+$ and $^{40}\text{Ar}^{12}\text{C}^+$) (Wang et al., 1999).

Table 3 lists the average relative analytic M/S error of the different chemical species in all analyzed

Fig. 1. M/S (measured-to-stimulated) ratio of elemental compositions for 25 samples.

Fig. 1. (Continued)

sample groups. As, Cd, Cr, Ni, Pb, Sb, V, and Zn analysis indicated high relative analysis error, especially Cd. A total relative analysis error of the 19 element species was 1.46–1.79 for the six group's particulate samples. There were insignificant differences between the six group samples in relative analysis error, but there were high errors in the A groups which may be attributed to three minor sources.

Lower measured recoveries in the Cd data (Fig. 1) may indicate the insensitivity of applied analytical techniques to trace amounts of chemical species. Based on Fig. 1 (E group), the sample mass did not significantly effect the analysis of sample composi-

tions, yet some elements had high variation i.e., Cd in E1, and Mg and V in E2.

3.2. Influence of analytical data's quality on CMB receptor model analysis

In a case study, the standard deviation for Al and Fe (non-marker species) was changed. The range of 5–30% corresponding to the change of source contribution was changed to 1–16% and all parameters (i.e., PMT, r^2 and χ^2 , etc.) fit the criteria of the model simulation. When the standard deviation of species analysis was over 30% the results of the model simulation were affected and did not meet the criteria. But few high standard deviations of non-mark species are measured in a high quality laboratory. Therefore, the non-mark species are not mentioned in the study (data not shown).

Table 4(a) shows the source contribution of each sample and the poor model identification for A3, B2, B4, C1, D2, E2 etc. Based on Fig. 1, the high analytic differences in sample composition response via the CMB model gave a low source contribution analytically. Most of samples had low Cd recovery in this study. In order to attempt to improve the source identification and fit the statistical criteria of

Fig. 1. (Continued)

Table 3
Relative analytic error of elements for different sample groups

Element	A $n = 4$	B $n = 4$	C $n = 4$	D $n = 3$	E $n = 3$	F $n = 7$	Average
Al	0.02 ± 0.02	0.03 ± 0.02	0.03 ± 0.01	0.03 ± 0.03	0.06 ± 0.03	0.03 ± 0.02	0.03
As	0.14 ± 0.07	0.11 ± 0.04	0.11 ± 0.02	0.13 ± 0.08	0.07 ± 0.05	0.24 ± 0.09	0.13
Ba	0.08 ± 0.04	0.07 ± 0.05	0.06 ± 0.03	0.09 ± 0.06	0.12 ± 0.04	0.01 ± 0.00	0.07
Ca	0.05 ± 0.04	0.05 ± 0.03	0.06 ± 0.02	0.04 ± 0.06	0.05 ± 0.04	0.03 ± 0.02	0.05
Cd	0.37 ± 0.36	0.35 ± 0.35	0.32 ± 0.13	0.33 ± 0.28	0.22 ± 0.14	0.11 ± 0.06	0.28
Cr	0.12 ± 0.07	0.07 ± 0.03	0.02 ± 0.02	0.12 ± 0.03	0.08 ± 0.06	0.13 ± 0.19	0.09
Cu	0.07 ± 0.07	0.05 ± 0.03	0.02 ± 0.01	0.04 ± 0.02	0.06 ± 0.06	0.04 ± 0.02	0.05
Fe	0.07 ± 0.02	0.07 ± 0.02	0.07 ± 0.01	0.08 ± 0.02	0.07 ± 0.02	0.04 ± 0.03	0.07
K	0.05 ± 0.03	0.04 ± 0.03	0.04 ± 0.02	0.07 ± 0.00	0.04 ± 0.03	0.04 ± 0.02	0.05
Mg	0.04 ± 0.03	0.14 ± 0.17	0.12 ± 0.08	0.03 ± 0.05	0.12 ± 0.16	0.02 ± 0.02	0.08
Mn	0.04 ± 0.04	0.04 ± 0.04	0.03 ± 0.02	0.04 ± 0.04	0.07 ± 0.05	0.03 ± 0.03	0.04
Na	0.09 ± 0.03	0.06 ± 0.03	0.05 ± 0.02	0.08 ± 0.01	0.10 ± 0.06	0.06 ± 0.03	0.07
Ni	0.13 ± 0.06	0.14 ± 0.04	0.14 ± 0.03	0.03 ± 0.03	0.06 ± 0.05	0.11 ± 0.12	0.10
Pb	0.14 ± 0.05	0.09 ± 0.03	0.08 ± 0.02	0.16 ± 0.02	0.11 ± 0.07	0.09 ± 0.08	0.11
Sb	0.16 ± 0.14	0.12 ± 0.08	0.11 ± 0.08	0.09 ± 0.013	0.05 ± 0.04	0.10 ± 0.06	0.11
Sr	0.01 ± 0.01	0.03 ± 0.02	0.01 ± 0.01	0.03 ± 0.01	0.06 ± 0.06	0.04 ± 0.02	0.03
Ti	0.03 ± 0.01	0.05 ± 0.03	0.02 ± 0.01	0.03 ± 0.04	0.05 ± 0.06	0.04 ± 0.03	0.04
V	0.06 ± 0.03	0.11 ± 0.08	0.09 ± 0.03	0.06 ± 0.03	0.11 ± 0.10	0.13 ± 0.06	0.09
Zn	0.12 ± 0.04	0.08 ± 0.04	0.08 ± 0.00	0.13 ± 0.00	0.08 ± 0.06	0.17 ± 0.07	0.11
Sum	1.79 ± 0.50	1.70 ± 0.27	1.46 ± 0.06	1.61 ± 0.61	1.58 ± 0.41	1.46 ± 0.15	1.60

Analysis by ICP-AES/ICP-MS.

Relative analysis error $\sum \left| \frac{M}{S} - 1 \right| / n$, n is number of samples.

Table 4

Composites	SRM 1648	BCR 176	SRM 2709	SRM 1633b	Analytic percentage	χ^2
(a) CMB simulation by using the analysis results of ICP-MS						
A1	69.3±2.9 (99) ^a	8.3±0.8 (83)	13.4±2.6 (134)	8.9±1.2 (89)	100.4	2.10
A2	-3.1±5.7 (-31)^b	73.6±2.7 (105)	14.9±6.1 (149)	11.5±3.2 (115)	93.2	1.15
A3	20.6±1.2 (206)	-0.5±0.2 (-5)	78.4±2.3 (111)	1.5±1.0 (15)	120.8	25.25
A4	11.4±1.6 (114)	7.7±0.5 (77)	11.9±1.9 (119)	69.0±2.1 (99)	99.5	1.71
B1	35.1±3.3 (88)	32.7±1.2 (109)	21.4±3.4 (107)	10.8±1.4 (108)	92.4	1.33
B2	45.9±2.3 (459)	1.8±0.6 (4.6)	50.8±3.3 (169)	1.5±1.6 (7)	141.3	28.05
B3	22.6±1.7 (113)	7.0±0.5 (70)	42.1±3.1 (105)	28.3±1.8 (94)	101.7	1.11
B4	22.3±2.6 (74)	16.1±1.1 (81)	35.2±2.6 (352)	26.4±1.5 (66)	111.6	4.63
C1	38.4±3.2 (116)	21.8±1.2 (66)	44.3±3.9 (134)	-4.5±1.8 (-)	109.0	4.95
C2	1.4±2.9 (-)	26.5±1.2 (80)	46.5±3.3 (141)	25.5±1.8 (77)	108.9	1.73
C3	31.4±3.3 (95)	0.3±1.2 (-)	36.1±3.8 (109)	32.1±1.9 (97)	96.8	0.84
C4	31.7±2.7 (96)	26.2±1.1 (80)	15.1±3.4 (-)	27.0±1.9 (82)	109.8	1.34
D1	35.5±3.9 (89)	38.7±1.7 (97)	16.9±4.0 (169)	8.9±1.9 (89)	101.2	1.94
D2	45.7±2.2 (114)	0.8±0.5 (8)	47.5±2.7 (119)	6.0±1.4 (60)	105.6	7.92
D3	37.8±3.8 (95)	9.6±1.4 (96)	13.6±3.5 (136)	38.9±2.2 (97)	99.9	0.73
E1	24.0±8.0 (96)	22.2±3.1 (89)	31.8±9.3 (127)	22.0±4.1 (88)	99.7	0.42
E2	25.1±2.2 (101)	19.4±0.9 (77)	35.8±3.2 (143)	19.8±1.7 (79)	120.0	1.19
E3	23.6±3.4 (95)	23.8±1.4 (95)	29.6±3.5 (118)	23.0±1.8 (92)	100.6	1.61
F1	34.8±3.0 (91)	17.7±1.2 (132)	11.5±3.1 (65)	35.9±1.8 (118)	88.3	3.84
F2	35.4±2.4 (104)	25.6±0.9 (98)	12.5±2.7 (68)	26.5±1.5 (124)	93.7	3.90
F3	15.5±3.4 (124)	43.3±1.5 (106)	20.2±4.0 (73)	21.1±1.9 (110)	88.5	3.20
F4	17.7±3.0 (95)	36.9±1.2 (111)	16.9±3.4 (73)	28.5±1.8 (115)	91.5	3.58
F5	29.3±3.0 (110)	28.8±1.2 (114)	2.1±3.4 (20)	39.8±1.9 (105)	88.6	4.06
F6	9.0±2.2 (75)	13.1±0.8 (104)	39.3±2.7 (105)	38.3±1.6 (102)	94.3	4.77
F7	24.4±2.5 (94)	13.5±0.9 (98)	36.6±2.9 (106)	25.5±1.6 (99)	99.2	6.21
Out of criteria (#)	6	9	16	7	2	8
(b) CMB simulation by using the analysis results of ICP-MS and IC						
A1	69.3±2.7 (99) ^a	8.4±0.8 (84)	13.4±2.6 (134)^b	8.9±1.2 (89)	100.3	1.77
A2	2.0±4.6 (20)	72.1±2.5 (103)	16.5±5.8 (165)	9.6±2.9 (96)	96.2	1.20
A3	17.7±1.0 (177)	-0.1±0.2	80.4±2.3 (115)	2.1±1.0 (21)	120.1	27.02
A4	10.7±1.3 (107)	7.9±0.4 (79)	12.1±1.8 (121)	69.3±2.1 (99)	99.1	1.47
B1	36.3±3.0 (91)	32.0±1.2 (107)	21.4±3.3 (107)	10.4±1.4 (104)	93.2	1.31
B2	38.9±1.9 (389)	3.7±0.5 (9.3)	53.7±3.2 (179)	3.7±1.5 (19)	137.1	30.50
B3	22.0±1.5 (110)	7.1±0.4 (71)	42.7±3.1 (107)	28.2±1.8 (94)	102.0	1.08
B4	23.1±2.2 (77)	15.8±1.0 (79)	34.8±2.5 (348)	26.2±1.5 (66)	112.0	3.90
C1	37.4±2.8 (113)	22.3±1.2 (68)	44.6±3.8 (135)	-4.3±1.8 (-)	108.7	4.19
C2	1.2±2.3 (-)	26.7±1.1 (81)	46.5±3.3 (141)	25.6±1.8 (78)	108.6	1.45
C3	31.3±1.9 (95)	0.0±0.4 (-)	36.7±3.4 (111)	32.0±1.8 (97)	97.2	0.71
C4	31.7±2.7 (96)	26.2±1.1 (80)	15.1±3.4 (-)	27.0±1.9 (82)	109.0	1.23
D1	35.2±3.4 (88)	38.2±1.5 (96)	17.6±3.9 (176)	8.9±1.8 (90)	101.5	1.71
D2	43.7±1.9 (109)	1.4±0.4 (15)	48.5±2.7 (121)	6.4±1.4 (64)	104.6	8.04
D3	38.9±2.8 (97)	9.2±1.0 (92)	13.6±3.3 (136)	38.3±2.1 (96)	100.8	0.68
E1	23.7±3.9 (95)	21.8±2.3 (87)	32.8±8.1 (131)	21.6±3.8 (87)	100.5	0.36
E2	23.3±2.3 (93)	19.9±0.9 (80)	36.7±3.2 (147)	20.0±1.8 (80)	119.1	1.16
E3	23.3±2.7 (93)	23.6±1.2 (94)	30.1±3.4 (121)	23.0±1.8 (92)	100.8	1.39
F1	37.4±2.2 (98)	16.6±1.0 (123)	11.4±2.9 (64)	34.6±1.7 (113)	89.6	3.38
F2	36.1±2.0 (106)	25.4±0.8 (97)	12.3±2.6 (67)	26.2±1.5 (122)	94.0	3.32
F3	15.5±2.7 (124)	43.1±1.4 (106)	20.5±3.9 (74)	20.9±1.8 (109)	88.8	2.71
F4	18.8±2.4 (101)	36.4±1.1 (109)	16.7±3.3 (72)	28.1±1.8 (113)	92.1	3.04
F5	29.7±2.4 (111)	28.5±1.1 (113)	2.3±3.3 (22)	39.5±1.8 (104)	89.0	3.44
F6	11.3±1.3 (94)	12.7±0.6 (100)	38.3±2.6 (102)	37.6±1.6 (100)	94.8	4.35
F7	25.4±1.7 (98)	13.3±0.8 (97)	36.1±2.8 (105)	25.2±1.5 (97)	99.6	5.71
Out of criteria (#)	5	8	18	7	2	6

Table 4 (continued)

Composites	SRM 1648	BCR 176	SRM 2709	SRM 1633b	Analytic percentage	χ^2
(c) CMB simulation by using the analysis results of ICP-MS, IC and spectrophotometer						
A1	70.9±2.8 (101) ^a	8.8±0.8 (88)	10.6±2.1 (106)	9.7±1.2 (97)	98.5	1.85
A2	1.6±4.8 (16)	73.2±2.3 (104)	10.5±3.3 (105)	11.1±2.7 (111)	92.6	1.20
A3	18.3±1.0 (183)^b	−0.1±0.2 (−1)	78.8±2.1 (113)	3.0±1.0 (30)	117.0	26.95
A4	10.9±1.3 (109)	8.0±0.4 (80)	11.6±1.8 (116)	69.4±2.1 (99)	98.3	1.49
B1	36.6±3.0 (92)	32.3±1.1 (108)	20.5±2.5 (102)	10.7±1.3	92.7	1.25
B2	44.9±2.1 (449)	4.5±0.6 (11.3)	42.5±2.6 (141)	8.1±1.6 (41)	123.1	31.71
B3	22.9±7.5 (114)	7.3±0.5 (73)	40.6±2.7 (102)	29.2±1.8 (98)	99.9	1.22
B4	24.0±2.4 (80)	18.5±1.1 (92)	29.4±2.2 (294)	28.1±1.6 (70)	105.7	6.37
C1	40.3±2.9 (122)	24.6±1.2 (75)	37.3±2.9 (113)	−2.3±1.7	102.4	4.53
C2	1.2±2.4	29.0±1.1 (88)	42.1±2.8 (127)	27.8±1.8 (84)	103.6	2.22
C3	32.2±1.9 (98)	0.0±0.4	34.9±2.8 (106)	32.9±1.7 (100)	95.9	0.75
C4	34.9±2.9 (106)	29.2±1.2 (89)	5.2±2.7	30.7±2.0 (93)	101.4	2.12
D1	36.5±3.6 (91)	41.7±1.6 (104)	10.6±2.6 (106)	11.2±1.8 (112)	96.4	1.87
D2	45.3±1.9 (113)	1.6±0.4 (16)	45.6±2.4 (114)	7.5±1.4 (75)	101.9	8.04
D3	40.1±2.8 (100)	9.8±1.0 (98)	10.3±2.7 (103)	39.8±2.1 (99)	98.3	0.81
E1	25.5±4.2 (102)	24.1±2.3 (96)	24.9±4.2 (100)	25.6±3.6 (102)	94.8	0.43
E2	25.5±4.2 (102)	24.1±2.3 (96)	24.9±4.2 (100)	25.6±3.6 (102)	109.6	2.9
E3	22.5±2.6 (90)	21.9±1.1 (88)	34.6±2.8 (138)	21.0±1.7 (84)	104.7	1.80
F1	37.1±2.2 (97)	16.3±1.0 (121)	12.7±2.4 (72)	33.9±1.6 (111)	90.5	3.26
F2	35.9±2.0 (105)	25.2±0.8 (96)	12.9±2.2 (71)	26.0±1.5 (121)	94.5	3.16
F3	15.2±2.6 (122)	41.8±1.3 (102)	23.4±2.9 (85)	19.6±1.7 (102)	90.6	2.68
F4	18.7±2.3 (100)	36.0±1.1 (108)	17.6±2.6 (76)	27.7±1.7 (112)	92.7	2.90
F5	29.0±2.3 (109)	27.6±1.0 (110)	5.1±2.6 (49)	38.3±1.8 (101)	90.8	3.40
F6	11.4±1.3 (95)	12.9±0.6 (101)	37.9±2.4 (101)	37.9±1.6 (101)	94.4	4.12
F7	25.9±1.8 (100)	13.9±0.8 (101)	33.8±2.4 (98)	26.4±1.5 (102)	97.6	5.52
Out of criteria (#)	4	6	9	6	1	7

^aValue in the parenthesis implies the relative percentage of model: simulation(mass of model simulation/mass in the particulate sample) × 100%.

^bBold mark indicates the data could not fit the criteria of model.

the CMB model, Cl^- , F^- and SO_4^{2-} were analyzed by IC and combined with the other 19 elements analyzed by ICP-MS. The results of the CMB model are shown in Table 4(b). These three additional ionic species did not enhance the model in identifying the pollution source. When a total of 23 species including Si was analyzed and measured by CMB, the model identification was enhanced significantly as shown in Table 4(c). Some of the samples (i.e., A3, B2, and C1), however, did not meet the model criteria. Therefore, the precision and accuracy of chemical sample species are important in the CMB model.

In order to improve the CMB source identification, some of the high variation and low recovery elements were removed from the chemical species i.e., Cd. Table 5 shows a typical case (A3); results indicated that the removal enhanced the identification of the CMB model significantly. Omitting the high variation and low recovery elements in most

cases better enhanced the model identification than by adding more analyzed species in the samples. Therefore, the precision and accuracy of analyzed elements are one of important factors which affect the model analysis.

To understand the influence of measured analytical data on the CMB results, the chemical species in the source profiles were further classified according to their concentrations and relative significance.

One of the classic problems of CMB models is that for many species, the many source composition patterns are so similar that it is difficult to resolve the concentrations. As illustrated in Tables 3 and 4, species having higher relative concentrations in minor sources are not helpful because their concentrations in simulated samples may be dominated by other sources. In fact, good source profile precision and accuracy of unique species ("marker" species, $M/S \approx 1.0$) have a great influence on the resolving ability of the CMB model.

Table 5
Sample A3 Cd removal from the element species

Analytic instrument	SRM 1648	BCR 176	SRM 2709	SRM 1633b	Analytic percentage	χ^2
ICP-MS	20.6 ± 1.2 (206) ^a	−0.5 ± 0.2 (−5)	78.4 ± 2.3 (112)	1.5 ± 1.0 (15)	120.8	25.25
ICP-MS (no Cd)	6.3 ± 1.7 (63)	10.7 ± 0.7 (107)	75.3 ± 2.7 (108)	7.7 ± 1.2 (77)	100.6	3.1
ICP-MS + IC	17.7 ± 1.0 (177)	−0.1 ± 0.2 (−1)	80.4 ± 2.3 (115)	2.1 ± 1.0 (21)	120.1	27.02
ICP-MS + IC (no Cd)	7.4 ± 1.3 (74)	10.4 ± 0.6 (104)	74.3 ± 2.4 (106)	7.9 ± 1.1 (79)	100	2.86
ICP-MS + IC + Si	18.3 ± 1.0 (183)	−0.1 ± 0.2 (−1)	78.8 ± 2.1 (113)	3.0 ± 1.0 (30)	117.0	26.95
ICP-MS + IC + Si (no Cd)	7.5 ± 1.3 (75)	10.0 ± 0.6 (100)	75.2 ± 2.6 (107)	7.3 ± 1.1 (73)	101.6	2.76

^aValue in the parenthesis implies the relative percentage of model: simulation(mass of model simulation/mass in the particulate sample) × 100%.

To evaluate the resolving ability of the CMB model on major, minor and non-existing sources, different groups' simulated samples were analyzed to apportion their source contributions, respectively. As seen in Table 4, the apportioned source contributions are generally in good agreement with the simulated values. On the other hand, significant fluctuations appeared on the estimated source apportionments of minor sources, which may indicate the existence of a serious collinear problem. It was noticed that NIST SRM 1648 and BCR No. 176, or NIST SRM 1633b and NIST SRM 2709 were not adequately resolved from each other during the analysis, even though their compositions were not identical. In fact, the sum of these two group's estimated major source contributions very closely approximates that of simulated contributions in D1 sample.

A major challenge to the application of the CMB model is to distinguish the non-existing and unknown sources, which have been included in the source profile of the model (Christensen, 2004; Christensen and Gunst, 2004). It was found from Table 4, that the sources not actually present generally yielded contributions less than their standard errors except for the C4 sample. In C4, the source contribution of the soil standard was overestimated since its prominent species was in common with the coal fly ash standard. Actually, the profiles of all standard sources were significantly distinct from those of other sources. As a result, overestimating the number of sources had little effect on the calculated source contributions if the "marker" species of non-existing sources were included in the calculation of source contributions.

Generally, the problem of collinearity is caused by the intercorrelation among the called "independent

species" (compositions of particulate samples). Although the intercorrelation among these variables is not extremely high, they usually significantly affect the results of CMB model simulation and lead to distortions in the results of the model. Therefore, some particulate source could be overestimation and some sources could be extinction while the collinearity problem in the pollution sources of particle. Table 6 shows the combined collinear source profiles which improved the model stimulation for C1 sample.

A quantitative deviation between the simulated and estimated source contributions can be calculated in terms of RPD (relative percentage difference):

$$\text{RPD}(\%) = \{|X_S - X_E|/\{(X_S + X_E)/2\}, \quad (1)$$

where X_S and X_E are the simulated and estimated source contributions, respectively.

It was found that the apportioned source's RPD values generally decrease with the extent of contributions. The RPD values of major sources can generally be controlled within 20%. Large deviations can only be observed for minor sources and be attributed to inaccurate analytical data as well as collinearity among sources.

3.3. Improving the CMB result by a two-step procedure

Ideally, one should use concentrations of all measured species in receptor modeling to obtain the source strength; however, in testing the CMB method, we can use the S/M concentration ratios of different species as a measure of the quality of the fit. A better CMB receptor model result can then be achieved by removing the data of species whose M/S

Table 6

A case study of combined colinearity sources

Composites	SRM 1648	BCR 176	SRM 2709	SRM 1633b	Analytic percentage	χ^2
ICP-MS	38.4±3.2 (116) ^a	21.8±1.2 (66)	44.3±3.9 (134)	−4.5±1.8 (−)	109.0	4.95
ICP-MS+IC	37.4±2.8 (113)	22.3±1.2 (68)	44.6±3.8 (135)	−4.3±1.8 (−)	108.7	4.19
ICP-MS+IC+Si	40.3±2.9 (122)	24.6±1.2 (75)	37.3±2.9 (113)	−2.3±1.7	102.4	4.53
M1		M2				
ICP-MS	69.8±1.7 (106)		30.2±0.6 (92)		101.3	3.63
ICP-MS+IC	69.8±1.7 (106)		30.2±0.6 (92)		101.3	3.09
ICP-MS+IC+Si	69.4±1.6 (105)		30.6±0.6 (93)		100.4	3.11

M1: SRM 1648 and BCR 176; M2: SRM 2709 and SRM 1633b.

Bold mark indicates the data could not fit the criteria of model.

^aValue in the parenthesis implies the relative percentage of model: simulation(mass of model simulation/mass in the particulate sample) × 100%.

Table 7

Variations of χ^2 values of prepared samples

Sample no.	All analyzed chemical species ^a	$ M/S-1 \leq \pm 20\%$	$ M/S-1 \leq \pm 15\%$	$ M/S-1 \leq \pm 10\%$
A1	1.85	1.22 (22) ^b	0.98 (19)	0.86 (16)
A2	1.20	1.20 (23)	1.12 (22)	0.67 (19)
A3	27.0	1.34 (18)	0.80 (11)	0.17 (10)
A4	1.49	1.41 (21)	1.24 (19)	1.24 (19)
B1	1.25	1.25 (23)	1.18 (22)	1.21 (21)
B2	31.7	2.82 (16)	0.41 (6)	0.78 (4)
B3	1.22	1.21 (22)	1.15 (21)	0.87 (18)
B4	6.37	3.78 (22)	0.58 (21)	0.15 (18)
C1	4.53	1.06 (21)	1.13 (20)	0.93 (17)
C2	2.22	2.17 (22)	1.13 (20)	0.31 (13)
C3	0.75	0.73 (22)	0.73 (22)	0.68 (21)
C4	2.22	2.22 (23)	1.35 (20)	0.50 (13)
D1	1.87	1.65 (22)	0.52 (19)	0.17 (16)
D2	8.04	0.70 (15)	0.70 (15)	0.67 (11)
D3	0.81	0.81 (23)	0.42 (20)	0.41 (16)
E1	0.43	0.25 (22)	0.25 (22)	0.20 (21)
E2	2.90	2.90 (23)	0.63 (17)	0.45 (14)
E3	1.80	1.80 (23)	1.65 (21)	0.58 (18)
F1	3.26	2.76 (22)	2.53 (20)	1.41 (14)
F2	3.16	3.16 (23)	2.74 (21)	1.86 (19)
F3	2.68	2.50 (22)	1.63 (21)	1.25 (19)
F4	2.90	2.69 (22)	1.60 (20)	0.58 (18)
F5	3.40	3.30 (22)	2.83 (20)	0.98 (17)
F6	4.72	2.12 (21)	1.99 (19)	1.34 (17)
F7	7.52	1.78 (19)	1.78 (19)	0.74 (18)

^a23 analyzed chemical species of samples.^bData presented in parenthesis is the number of chemical species input for CMB model.

values are apparently deviating from 1. For example, in this experiment, Cd was the element whose analytical data was not accurate and should not be placed in the model analysis. Table 5 shows that when the low Cd recovery was not included in

the A3 CMB model, there was a significant increase in the resolution of source contribution.

Table 7 shows the χ^2 values of the primary CMB results analyzed from various samples and the removal of the chemical species from the input data

with $(M/S-1)$ values over $\pm 20\%$, $\pm 15\%$ or $\pm 10\%$, respectively. We demonstrate, through the examination of these samples, that the χ^2 values decrease generally with removing the less precise chemical species from the model input data. Significant improvements were observed for samples of A3, B2, D2 and F7 (Fig. 1), in which data of the most eight inaccurate species ($|M/S-1| \leq 0.20$) had been initially removed. However, insignificant improvements for χ^2 values were also observed if further chemical species were removed ($|M/S-1| \leq 0.15$). Obviously, the resolving ability of the model is affected by the precision and accuracy of the input data and can be improved by removing inaccurate analytical data.

We found that the reduction of inaccurate or lower precision analytical data not only improves the statistical deviation of the model result, but also increases the capability of individual source apportionment. However, further reducing the number of chemical species without any criteria may insignificantly improve the statistical fluctuation but at the same time degrade the resolution of source contributions. In this investigation, the optimal criteria to select the acceptable analytical data will be those important “marker” species of pollution sources with M/S values close to one. The χ^2 values of all CMB results should also be controlled within 4. In real sample analysis, the actual source contributions are unknown; however, we still can predict the concentration of each species from the primary CMB results and estimate the predicted-to-measured ratio as data acceptable criteria.

As a result, a two-step modeling procedure, which first compares the measured analytical data to the one that was calculated from source contributions of primary CMB results, and then eliminates those non-marker and lower precise chemical species improved the capability of CMB model analysis. While the proposed two-step CMB modeling approach cannot be directly verified in real sample analysis, the evaluation of randomly prepared samples in group “F” may give some insight into the effectiveness of this procedure.

4. Conclusions

A set of simple four-source simulated samples was systematically employed to test the capability of CMB receptor model. These tests with 23 commonly measured chemical species showed that different source-types can be apportioned with

uncertainties less than 20% if accurate determinations of chemical species in both source and ambient samples are performed. Furthermore, better performance was demonstrated with the presence of unique “marker” species such as Si for soil or soluble chlorine for waste incineration ash in urban area. Although the chlorine could have come from sea salt or vegetable burning in rural area. It was found in this study that urban particulates and waste incineration ash source profiles, or soil and coal fly ash source profiles were collinear with the measured species. With lower source contributions, the capability of CMB receptor to apportion the sources was significantly degraded due to the influence of chemical species with lower precision in both the source and receptor measurements. Modeling results would be deteriorated with the existence of lower precise or inaccurate species, such as Cd. A proposed two-step modeling procedure, which first verifies the measured data from the source contributions of primary (first step) CMB results and then eliminates those chemical species with lower precision in the second step to obtain better a CMB result, has been demonstrated to effectively improve the capability of CMB model analysis. In addition, the effect of organic and cation species on the model simulation could be an important issues in the future study.

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