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Estimation of Source Contribution for PM10 by Chemical Mass Balance(CMB) in Busan

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Abstract

PM10 samples were collected from July 2007 to Oct. 2007 at Gwaebopdong(inland area) and Dongsamdong (coastal area), in Busan. This paper investigates the contribution of emission sources to PM10 mass in Busan. Source apportionment results derived from the chemical mass balance(CMB) method. A source profiles applied in this study is organized to minimize the collinearity among sources type via statistical method. Source profiles applied in this study utilized a measured value of fine particle directly sampled from metropolitan area such as Seoul and Incheon, After a CMB modeling, sulfate and nitrate related sources among those contributing to PM10 in Busan showed high contribution by 36.53% in Gwaebopdong and 42.02% in Dongsamdong.

Key Words : Chemical mass balance(CMB), Source apportionment, Source profiles, Sulfate and nitrate related

1. Introduction

It is very important to understand quantitatively or qualitatively all sorts of emission sources that affect concentration of air pollutants as air quality management. As a means of access, two models are organized. One is a dispersion model which evaluates its effect centering around emission source and the other is a receptor model that accurately estimates the influence of emission source in a receptor.

The dispersion model, a means that estimates the impact of emission source in a receptor using emission source data and meterological parameters, is widely used for estimation/assessment of the air in particular area and Environmental Impact Assessment.

However, field experiment and dynamic study on physical/chemical reaction among pollutants for the determination of emission source investigation and collection of meteorological data should be preceded to utilize a dispersion model. In the process, the dispersion model shows such weak points as an error of emission data, uncertainty of dispersion parameters, difficulty of understanding complicated features of diffusion and dispersion in the air.

Source apportionment of particulate matter is conventionally attempted using receptor-oriented models such as the chemical balance mass(CMB) model, which infers source contributions by determining the best-fit combination of emission source chemical composition profiles needed to reconstruct the chemical composition of ambient samples[1]. Application of a receptor model in atmospheric science gradually extends from a micro scale such as indoor air pollution to a local scale such as understanding of metropolitan pollution source and visibility reduction to a global scale such as acid rain and Asian dust. CMB is a method that estimates mass contribution by using a matrix of chemical element in air particulate and a matrix of source profile based on mass balance and law of mass conservation[2,3]. The object of this study shall be to provide basic data for effective management of the air

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quality by estimating contribution of pollution source to fine particles in Busan using CMB.

2. Chemical Mass Balance(CMB) model

The CMB model consists of a least-squares solution to a set of linear equations that expresses a receptor concentration of a chemical species as a linear sum of products of sources profiles species and source contributions. The fundamental concept of CMB is a mass balance of analyzed substances and a law of mass conservation. It can be expressed in a series of linear regression equations[4,5]. Contribution of pollution source is assessed by a least squares multiple linear regression method as shown in expression (1).

$$X_{ij} = A_{ik}F_{kj} \qquad (1)$$

Where, X*ij* is concentration of *i*th chemical species measured in a *j*th sample, A*ik* is mass fraction of *i*th chemical species discharged from *k*th emission source, F*kj* is mass concentration or mass contribution of *k*th pollution source.

The CMB model assumptions are[6~8]:

(1) Compositions of source emissions are constant over the period of ambient and source sampling.

(2) Chemical species do not react with each other, i.e, they add linearly.

(3) All sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized.

(4) The source compositions are linearly independent of each other.

(5) The number of sources of source categories is less than or equal to the number of chemical species.

(6) Measurement uncertainties are random, uncorrected, and normally distributed.

CMB receptor model in this study is CMB 8.2 developed by EPA in the U.S.A[9]. By means of CMB, principal pollution source of fine particles which affect a receptor can be found and each contribution for emission sources can be quantified. Also, an estimated value can be diagnosed by a verification method provided by CMB itself. After CMB is carried out into effect by using receptor concentration, SCE(Source Contribution Estimation), standard deviation of pollution source contribution, and concentration of chemical species are shown as the first result. And mass, Chi-square(χ^2), R-square(R^2) are computed followed by as statistical values to confirm whether concentration of chemical species is well designated. CMB also represents Ratio(C/M), Ratio(R/U), etc that help confirm to estimate the utmost value and shows a range of interpretation on model stability in Table 1. Fig. 1 shows PM10 sampling site in Busan.

Table 1. CMB performance measures

Parameter	Target
R square	0.8 to 1.0
Chi square	< 4.0
Percent mass	80 to 120
Degree of freedom	> 5
T-statistic	> 2.0
Ratio(Calculated/Measured)	0.5 to 2.0
Ratio(Residuals/Uncertainties)	-2.0 to 2.0

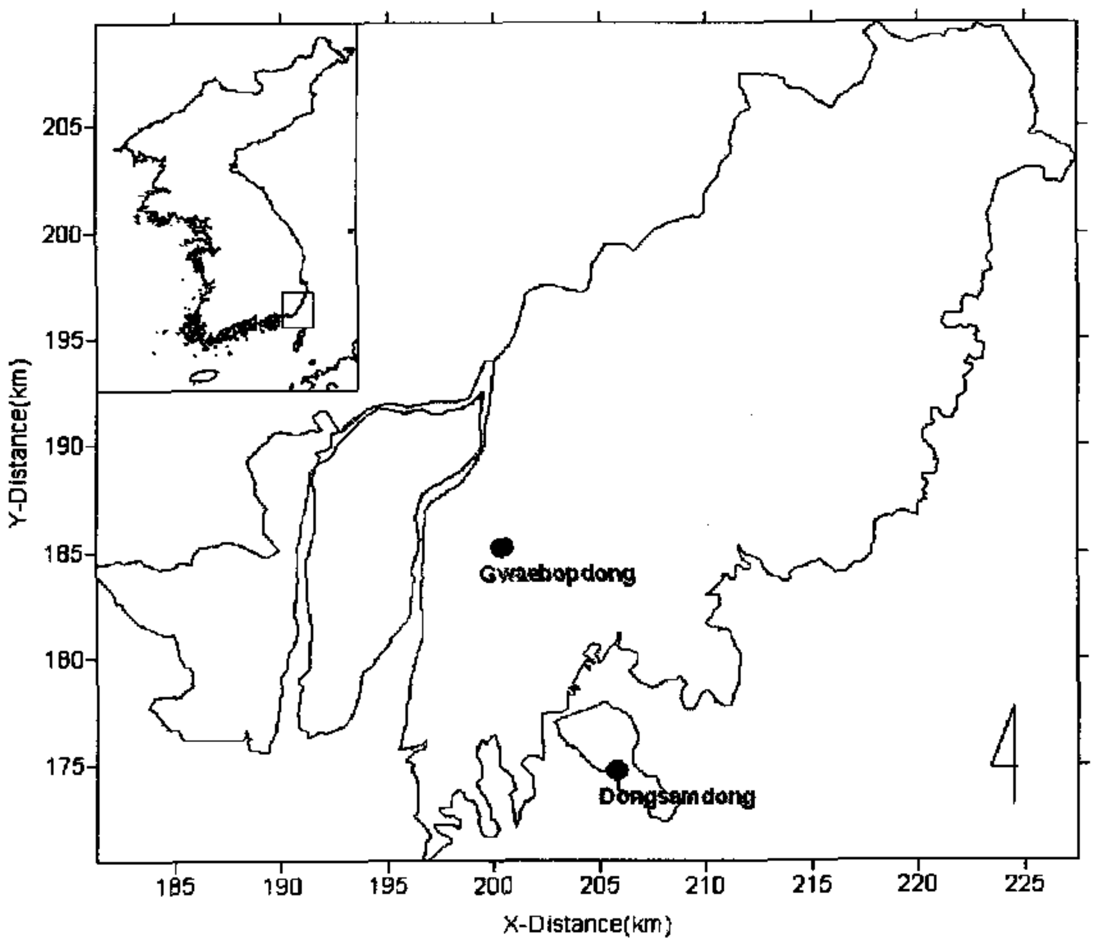

Fig. 1. PM10 sampling site in Busan.

3. Result and Discussion

3.1 Source profile

Accurate source profile are very important as to estimate the contribution of each sources by a receptor model. Although apportionment of source constituents is a crucial course during the application of a receptor model, South Korea currently uses a source profile produced by EPA(U.S). However, confidence of a receptor model gets depreciated when foreign data are used since domestic source profile are not properly reflected.

This study utilized a study result of NIER[10] which took features of domestic metropolitan source profiles into consideration to increase accuracy of a receptor model at the greatest. As this study has estimated a component ratio based on a fine particle extracted directly from Seoul, a feature of emission source is similar to that of Busan, the object area of this study, and the result is much more trustworthy in comparison with that of EPA. Table 2 shows each emission sources and major constituents to estimate contribution of sources for fine particle in Busan and total emission sources type are 11.

A source profiles, a main input data of CMB, can induce a error on contribution of sources when mutual independence among sources are not ensured. Collinearity among source types means the dependence among sources during the application of CMB, and it is the opposite conception of independence. Accordingly, it is essential to organize a source profile lest collinearity of each source should exist when framing it as an input of CMB.

A source profiles applied in this study is organized to minimize the collinearity among sources type via statistical method such as SVD(Singular Value Decomposition) regarding sources and components and the application of these data made possible more reliable estimation of contribution. Although a source profiles applied in this study utilized a measured value of fine particle directly sampled from Seoul and Incheon, other domestic study results were needed to be referred since contribution of diesel car and sea salt particle among sources were overestimated in the study. In addition, metal related out of total 11 sources types were divided into ferrous metal and non-ferrous metal according to source data produced by EPA, and soil related were classified into natural soil and road dust when applying the source profiles. Table 3 shows the source profile for PM10 lastly applied in this study.

Table 2. Major constituents of source types

	Emission sources	Major constituents
1	Oil related	EC, SO_4^{2-},Fe
2	Coal combustion	SO_4^{2-}, NO_3^-, S, Zn, OC, Ca
3	Motor vehicle	EC, OC, SO_4^{2-}, NH_4^+
4	Motor vehicle	EC, OC, SO_4^{2-}
5	Metal related	OC, Fe, Zn
6	Municipal incinerator	Cl, Zn, Pb, NO_3^-
7	Biomass/field burning	OC, EC, Zn, Pb, NO_3^-
8	Soil/road dust related	Si, Al, Fe, Mg, Ca, K
9	Aged seasalt	Na, Cl, SO_4^{2-}
10	Secondary sulfate	SO_4^{2-}, NH_4^+
11	Secondary nitrate	NO_3^-, NH_4^+

3.2. Verification of validity on CMB model result

The concentration of samples collected from each site was used to estimate contribution of fine particle in Gwaebopdong, and Dongsamdong, the receptor point(Fig. 1). Total number of samples in Gwaebopdong were 37, and normally extracted 35 data of which the model results were used to estimate contribution. Total number of samples in Dongsamdong were 29, and every sample was used to estimate contribution. There are various methods to verify a result of CMB, and such methods are suggested in Table 1.

CMB 8.2 used in this study can calculate the estimated result within statistically valid range via fitting process on each measurement data. In this study, manual fitting process on each datum was practiced, and Chi-square(χ^2) and R-square(R^2), diagnostic elements that are basically used during the verification process, were shown at Fig. 2 and Fig. 3. After manual fitting process was practiced on each data of this study, it showed that the variables come under statistically significant range.

R-square(R^2) showed a range of 0.96 ~ 1.00 and performance criterion(>0.8) by an average 0.99 in Gwaebopdong, and Dongsamdong showed a range of 0.97 ~ 1.00, and also performance criterion by an average 0.99. Chi-square(χ^2) showed a range of 0.00 ~ 3.84, and performance criterion(<4) by an average 2.18 in Gwaebopdong, and Dongsamdong showed a range of 0.04 ~ 3.83 and also performance criterion by an average 1.42.

Table 3. Source profile matrix for PM10

Element	Coal combustion	Municipal incinerator	Oil related	Diesel vehicle	Gasoline vehicle	Sea salt	Biomass burning	Soil	Road dust	Ferrous metal industrial	Non-ferrous metal industrial	Secondary sulfate	Secondary nitrate
Al	2.70	0.42	0.00	0.00	0.01	0.00	0.01	6.45	6.46	0.28	5.29	0.00	0.00
Fe	3.57	3.41	0.00	0.04	0.02	0.00	0.08	4.40	4.49	5.92	2.63	0.00	0.00
Mg	1.96	0.33	0.00	0.03	0.00	3.95	0.05	0.91	0.91	2.53	0.00	0.00	0.00
S	3.06	1.45	0.00	0.76	0.81	0.25	0.41	1.45	1.50	1.24	5.81	24.27	0.00
Si	15.04	0.25	0.00	0.63	1.85	0.04	0.12	17.14	15.41	0.13	0.00	0.00	0.00
Ti	0.17	0.03	0.00	0.00	0.00	0.00	0.00	0.57	0.52	0.17	0.12	0.00	0.00
Mn	0.14	0.01	0.00	0.00	0.00	0.01	0.00	0.16	0.11	0.46	0.32	0.00	0.00
Ba	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.01	0.20	0.00	0.00
Sr	0.11	0.06	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.04	0.00	0.00
Zn	3.46	1.18	0.00	0.05	0.10	0.01	0.04	0.16	1.97	6.94	17.70	0.00	0.00
V	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.04	0.00	0.00
Cr	0.11	0.07	0.00	0.00	0.00	0.00	0.02	0.02	0.04	0.09	0.03	0.00	0.00
Pb	0.15	0.37	0.00	0.01	0.08	0.00	0.00	0.60	0.20	0.07	9.71	0.00	0.00
Cu	0.24	0.26	0.00	0.01	0.73	0.00	0.00	0.03	0.08	0.16	0.42	0.00	0.00
Ni	0.19	0.12	0.00	0.02	0.01	0.00	0.01	0.01	0.15	0.22	0.18	0.00	0.00
Co	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.05	0.00	0.00
Mo	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.02	0.07	0.00	0.00
Cd	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	11.42	0.00	0.00
Cl^-	0.74	12.25	2.91	3.17	0.02	26.15	3.77	0.64	0.34	3.87	4.31	0.00	0.00
NO_3^-	0.20	1.24	0.00	0.19	0.00	0.00	0.06	3.35	0.03	4.34	0.55	0.00	77.50
SO_4^{2-}	7.21	3.06	3.81	1.48	0.14	0.71	2.83	3.90	0.42	4.89	16.00	72.70	0.00
Na	0.54	5.29	1.95	0.13	0.03	18.59	1.89	0.91	1.83	1.15	0.00	0.00	0.00
NH_4^+	0.79	0.56	0.82	0.26	0.02	4.19	0.47	2.35	0.15	0.39	0.00	27.30	22.55
K	0.72	3.64	0.27	0.08	0.00	0.04	6.79	1.81	1.38	2.20	1.74	0.00	0.00
Ca	3.96	6.64	1.69	0.09	0.30	0.34	0.20	1.85	3.88	8.79	1.14	0.00	0.00
OC	1.61	3.56	5.66	25.30	71.08	0.02	32.95	9.84	11.68	1.88	13.00	0.00	0.00
EC	0.29	1.26	35.65	54.46	2.95	0.00	2.20	3.38	1.54	0.15	0.00	0.00	0.00

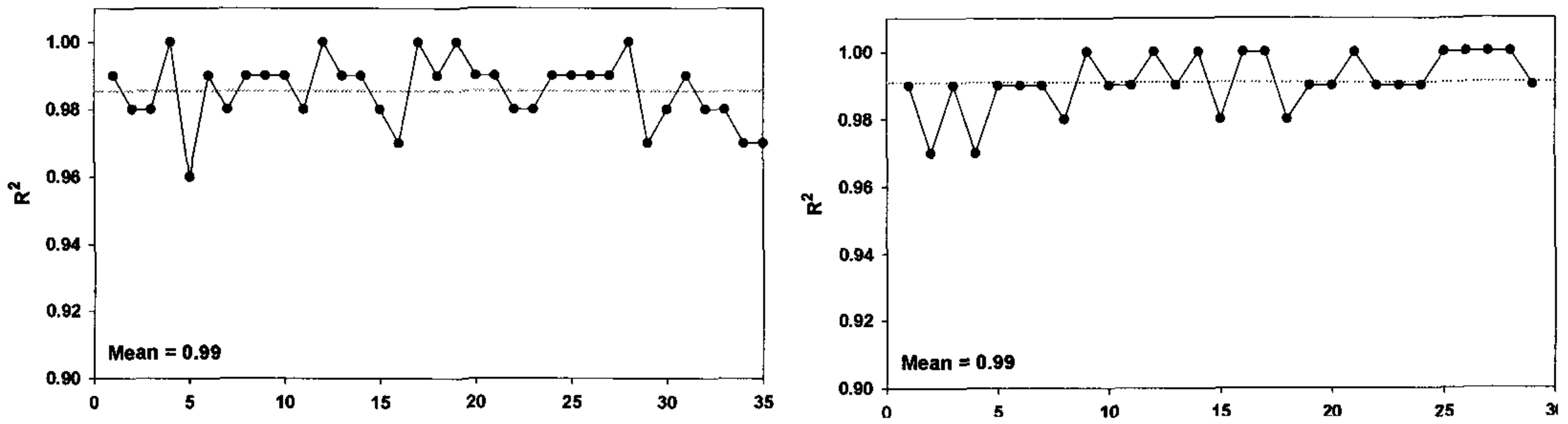

Fig. 2. R-square of CMB modeling result at the two sampling site in Busan. (Above : Gwaebopdong, Bottom : Dongsamdong)

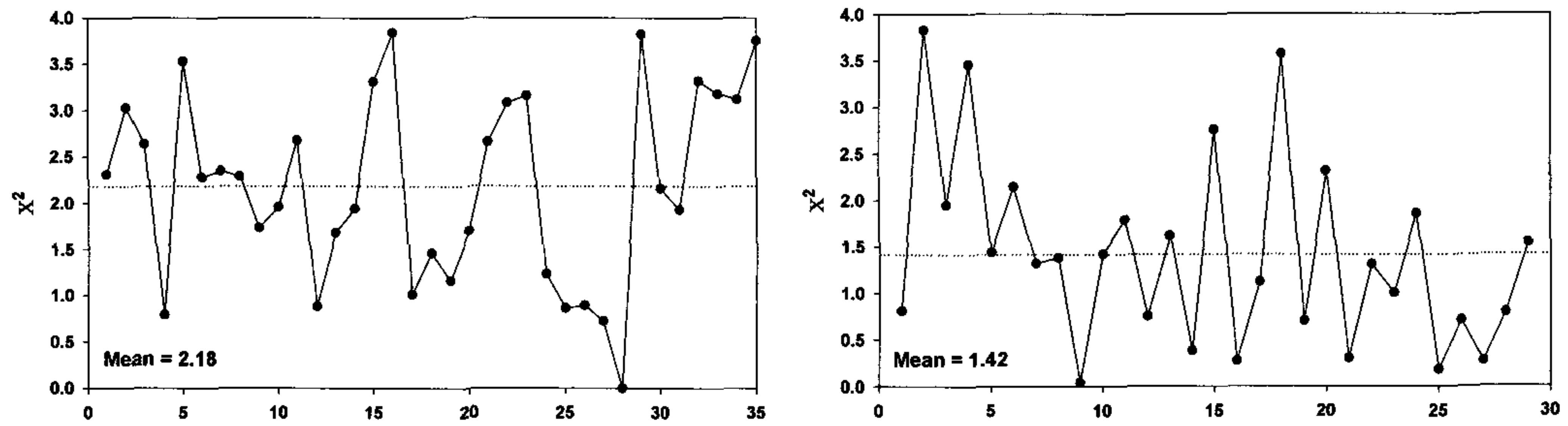

Fig. 3. Chi-square of CMB modeling result at the two sampling site in Busan. (Above : Gwaebopdong, Bottom : Dongsamdong)

Table 4. Average source contribution for PM10 at the two sampling site in Busan

Sources	Gwaebopdong		Dongsamdong	
	Concen.($\mu g/m^3$)	Contri.(%)	Concen.($\mu g/m^3$)	Contri.(%)
Oil related	1.02	2.65	0.01	0.02
Coal combustion	1.69	4.38	2.30	5.60
Diesel vehicle	3.75	9.73	7.38	17.99
Gasoline vehicle	2.29	5.94	1.27	3.09
Metal related	1.17	3.04	1.56	3.78
Municipal incinerator	4.20	10.91	0.97	2.36
Biomass/field burning	5.21	13.52	0.99	2.41
Soil/road dust related	2.67	6.96	3.60	8.78
Aged seasalt	2.44	6.34	5.72	13.95
Secondary sulfate	4.93	12.79	10.49	25.57
Secondary nitrate	9.14	23.74	6.75	16.45
Total	**38.51**	**100.00**	**41.04**	**100.00**
Measure mass	70.74		64.27	
Calculate mass	38.51		41.04	
R-square	0.99		0.99	
Chi-square	2.18		1.42	
Percent mass(%)	55.23		58.05	

3.3. Result of source contribution

Table 4 showed average source contribution for PM10 at the two sampling site(Gwaebopdong and Dongsamdong) from July 2007 to Oct. 2007 in Busan. Although Chi-square(χ^2) and R-square(R^2), the diagnostic elements that verify the result of CMB, turned out to satisfy the performance criterion, percent mass(%) which shows the rate of computed value regarding measured value of PM10 concentration exceeded confidence level ±20% by an average 55.23% in Gwaebopdong and 58.05% in Dongsamdong. This was caused by the elements of primitive measurement data on PM10 occupying about 65% in Gwaebopdong and 74% in Dongsamdong of actual PM10 mass concentration. However, since sources contribution does not always corresponds to analytic standard, contribution of each source was estimated by having the sum of it, 100.

In Gwaebopdong, mean concentration of PM10 was 70.74 $\mu g/m^3$, and a calculated value was 38.51 $\mu g/m^3$. Emission sources regarding secondary particle and biomass burning/illegal incineration out of 11 sources were estimated to be main sources in Gwaebopdong. That is, secondary nitrate showed the highest value, 23.74% and biomass/field burning and secondary sulfate showed similar contribution, 13.52% and 12.79%, respectively. In addition, considering that season of this study was autumn, it shows similar results in comparison with the existing study result, which shows high contribution by biomass burning in autumn. Contribution of automobiles were estimated to be 15.67%. Partly, diesel vehicle showed 9.73% and gasoline vehicle showed 5.94%, which is about 1.6 times lower than that of the former ones. The contribution of a soil/road dust source, a crust oriented source, turned out to be 6.96% which is higher than that of gasoline vehicle. In case of sea salt, expected to affect Busan area, its contribution came out as 6.34%.

In Dongsamdong, mean concentration of PM10 came out somewhat lower than that of Gwaebopdong, but its calculated value was 41.03 $\mu g/m^3$. Dongsamdong also showed contribution of secondary aerosol highest, 42.02% just like Gwaebopdong, and sulfate and nitrate accounted for 25.57% and 16.45%, respectively. The second high contribution was automobile. Total contribution of automobiles was 21.08% and the contribution showed a big difference according to different car fuels, diesel vehicle as 17.09% and gasoline vehicle as 3.09%. The phenomenon that contribution of diesel vehicle in Dongsamdong appears high is thought to be due to source emitted from boats sailing the coast around a sampling site or from ships at anchor. Contribution of sea slat on PM10 in Dongsamdong is 13.95%. Accordingly, influence of sea slat in areas adjacent to the coast like Dongsamdong is over 2 times higher than that in an inland area, Gwaebopdong (6.34%). Hence, sea slat which contributes to the concentration of PM10 in Busan affects about 10% in a coastal area and 5% in an inland area. The contribution of soil related sources in Dongsamdong appeared 8.78%, which is about 2% higher than that in Gwaebopdong. Next, the contribution of coal combustion sources came out as 5.60%, that of industrial process as 3.78%, and lastly that of incinerator as 2.36%. Coal combustion and industrial process showed similar contribution with that of Gwaebopdong, but incinerator showed much lower contribution compared to over 10% contribution shown in Gwaebopdong. Dongsamdong appeared different from Gwaebopdong by having contribution of biomass/field burning as 2.41% and turned out to have a rare influence by having contribution of fossil fuel combustion as 0.02%.

After a CMB modeling, sulfate and nitrate related sources among those contributing to PM10 in Busan showed high contribution by 36.53% in Gwaebopdong and 42.02% in Dongsamdong. Therefore, a intensive investigation on formation mechanism of a secondary aerosol in Busan and a management strategy are required.

4. Conclusions

The source contribution on PM10 in Busan using CMB model developed by EPA is summarized as follows.

In Gwaebopdong, a calculated value of PM10 was 38.51 $\mu g/m^3$. Also, a secondary nitrate appeared highest, 23.74% and a biomass/field burning and a secondary sulfate showed similar contribution, 13.52% and 12.79%, respectively. Diesel vehicle marked 9.73%, gasoline vehicle 5.94%, and soil/road dust related which are crust oriented emission sources 6.96%.

In Dongsamdong, a calculated value of PM10 was 41.03 $\mu g/m^3$ and contribution of secondary aerosol marked highest, 42.02% just as in Gwaebopdong. Especially, a sulfate showed 25.57% and a nitrate showed 16.45%. Total contribution of automobiles was 21.08% and contribution of sea salt marked 13.95%, which was over 2 times higher than that of an inland area. Soil related showed contribution of 8.78%, a coal combustion as 5.60%, an industrial process as 3.78%, and a municipal incinerator as 2.36%.

As a result of CMB modeling, a sulfate related and a nitrate related source out of those contributing to PM10 in Busan, showed high contribution by 36.53% in Gwaebopdong and 42.02% in Dongsamdong, respectively.

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