SOURCE APPORTIONMENT OF VOC$_S$ BY RECEPTOR MODELLING IN AN URBAN SITE IN HA NOI

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ABSTRACT

Volatile organic compounds (VOCs) are atmospheric pollutants of concern because of the health effect including carcinogenic risk of some of their species and the contribution in the formation of tropospheric ozone. The levels of VOCs in Hanoi were demonstrated to be higher than neighboring countries by previous research. The ozone potential formation (OFP) of VOCs was also some folds higher than others. Among transportation sources, VOCs were proved to be mainly emitted from motorbikes. The contribution percentages of transportation and other sources such as industrial, biomass burning sources are still remained unknown. In this research we applied chemical mass balance (CMB) receptor modelling to determine VOCs source apportionment. One week VOCs observation data at Hanoi University of Science and Technology in June 2017 was applied for investigation. Fourteen VOC species among 55 of which were applied for CMB modelling. Transportation and biomass burning source profiles were developed by monitoring in this study. Four other source profiles, namely gasoline evaporation, industrial production, cooking and paint that were compiled or calculated from previous studies. The results showed that the main sources of VOCs were vehicular emission, biomass burning, and gasoline evaporation contributing 37 %, 21 % and 20 % for VOCs levels, respectively. Other sources contributed for the leftover. The results can support to initiate policy for future control of VOCs.

Keywords: VOCs, source profile, GC-FID, receptor modelling, CMB.

1. INTRODUCTION

Volatile organic compounds (VOCs) are one of major concern in air pollution. Some species of VOCs such benzene, and ethylbenzene are considered as very toxic substances for human health. VOCs participate in photochemical reactions forming tropospheric ozone. They also contribute in forming secondary particulate matters. The total VOC (TVOC) and total ozone formation potential (OFP) in a street in Hanoi were 374 (μg/m^3) and. 1308 (μgO$_3$/m^3), respectively [1]. Sakamoto *et al.*, 2018 reported that TVOC and total OFP were 50.25 ppb and 308.7 ppb (O$_3$), respectively [2]. The high levels of VOCs will require suitable abatement method in order to control VOCs in the future. However, there was no information about VOCs apportionment except for the evidence that transportation is the dominant source of them. This research aims at carrying source apportionment for VOCs in Hanoi for the first time.

VOC apportionment can be done by applying receptor models. Chemical Mass Balance (CMB) model which is developed by US Environmental Protection Agency (US-EPA) has been used for source apportionment of VOCs by many studies [3-5]. In order to apply CMB model, the profiles of emission sources are required. Phuc and Kim Oanh [6] reported that BTEX (the major compound group among VOCs) were attributed by gasoline fueled vehicles, following by residential cooking, open burning of solid waste and agricultural residues, loading and refueling activities at gasoline stations, and industry located inside cities. In this study, six source profiles were selected including vehicular emission, biomass burning, gasoline evaporation, industrial production, cooking and paint.

2. MATERIALS AND METHODS

2.1. VOCs sampling and analysis

2.1.1. Ambient VOCs sampling

VOCs sampling was carried at Hanoi University of Science and Technology (HUST) (21°0 ′19 ″N, 105°50 ′43 ″E) in Hanoi, Vietnam. The site was described elsewhere [2]. Forty samples were collected by sorbent-filled cartridges (C3-CXXX-5035, Markes International Ltd., U.K.) at flow rate of 0.2 L min^{-1} for 10 min at 2:00 am, 8:00 am, 2:00 pm, 6:00 pm from 20th to 28th of June 2017. Fifty-five VOCs were analyzed by GC-FID. Details of analysis methods and data processing were introduced elsewhere [2]. It was noted that the sampling time was at the lagging period of biomass burning in Hanoi and nearby area.

2.1.2. VOCs emission source sampling

Roadside and biomass burning samples were conducted to determine traffic and rice straw burning emission profiles in Hanoi. Six roadside samples were taken on the pavement of Dai Co Viet street at 1.8 meter height at the same sampling flowrate and duration with the ambient ones at 8:00am, 2:00pm, 6:00pm on 21st and 26th June 2017. Four rice straw burning flume samples were carried out at four fields on 22nd and 25th June 2017. These samples were taken at flow rate of 0.1 L min^{-1} in 2 min, some meters down flow from the plume.

2.3. Receptor modelling

CMB model was used to estimate the contributions of different potential emission sources. It requires two data sets for estimating: (1) ambient measurement data and (2) source profiles. A

CMB model correlates previously determined source profiles to measured receptor concentrations, solving the multiple regression equation:

$$C_t = F \times S_t + \varepsilon_t \tag{1}$$

where C_t is the vector of the VOC species' concentrations quantified in one sample taken at time t, F is the source profile matrix, S_t is the source contribution vector, and ε_t is the error vector. The source profile matrix F is composed of previously measured source profile vectors, with each vector describing the relative contents of VOC species (in ppbC %) from the respective sources. The source contribution vector, which is the unknown of this equation, is the absolute contribution of each source to the total measured ambient VOC concentrations (in ppbC) [3].

CMB version 8.2 (developed by US-EPA), the most widespread version of this model, was applied in this research. The criteria given in US-EPA (2004) were applied for the results of this research: $R^2 \geq 0.8$, $\chi^2 \leq 2$, 80 % $\leq$ modeled to measured mass ratio $\leq$ 120 %, standard errors $\leq$ 1/2 times the source contribution estimate, and projection into eligible space for all sources = 0.95 [7].

In this study, the average concentration of VOCs in ambient sample at 6 pm was used as input data. Fourteen VOC species were selected for source apportionment analysis. Those species are typical tracers of various emission sources and to be the most abundant ones in receptor samples. Species that are highly reactive or high uncertainty were excluded, because they quickly react in the atmosphere, and to be significantly degraded on their way from the source to the receptor [4, 5].

3. RESULTS AND DISCUSSION

3.1. Ambient VOCs measurement data

Average TVOC concentration of all samples was 44.79 ppb, which is within the range of TVOCs in previous research in 2015 [2]. TVOC concentration was highest at 6 pm, at 63.74 ppb, followed by those at 8 am and 2 pm, at 52.83 ppb and 32.58 ppb, respectively and was lowest at 2 am, at 30.8 ppb. Among VOC species, the levels of highly concerned BTEX group, which includes benzene, toluene, ethylbenzene and xylenes were 3.35-13.19, 6.03-50.16, 0.74-10.9, 2.69-27.96 $\mu g/m^3$, respectively. Benzene concentrations in the present research were comparable with those in the research of Phuc and Kim Oanh (9 ± 4 $\mu g/m^3$) [6] but much higher than those in the research of Ha *et al.* (< 5 $\mu g/m^3$) [8]. Toluene, ethylbenzene, xylenes concentrations were in the same range with those in research of Phuc and Kim Oanh [6]. Toluene, xylene concentrations were several times lower than the results' research of Ha *et al.* [8]. Ethylbenzene concentrations were not detected in the research of Ha *et al.* [8]. The difference of BTEX concentrations between this research and the research of Ha *et al.* might be caused from the differences in sampling periods and positions. Whereas this sampling was taken at an urban site, far from main roads, the outdoor sampling positions in the research of Ha *et al.* were outside of houses which can be closed to VOC sources (*e.g.* roads). VOC concentrations in this research had the pattern that concentrations were high at traffic rush hour periods (6 pm and 8 am) and agriculture burning period (normally in the late afternoon). This fact implied the importance of traffic and biomass burning sources. Profiles of those sources, therefore, were developed in this research for CMB model application. Full data of ambient measurement will be presented in another paper.

3.2. Source profiles applied for CMB calculation

In this study, vehicular and biomass burning emission profiles were developed by monitoring. Other source profiles were selected or calculated from the literature. Summary of all source profiles is presented in Table 1.

Vehicular emission profile is shown in Figure 1. The most abundant species was toluene, accounted for 13 %, following were 1,2,4-trimethylbenzen, m,p-xylene, o-xylene with 11 %, 8 % and 6 %, respectively. Cao *et al.* [9] also reported that toluene accounted for the largest proportion (11 %), and following by i-pentane, benzene, and xylene. Figure 2 shows biomass burning emission profile. Ethane and propylene contributed the largest part of 16 % and 9 %, respectively. Following were toluene, benzene, n-octane of 8 %, 6 % and 3 %, respectively. The results are similar to a published research in China [10, 11].
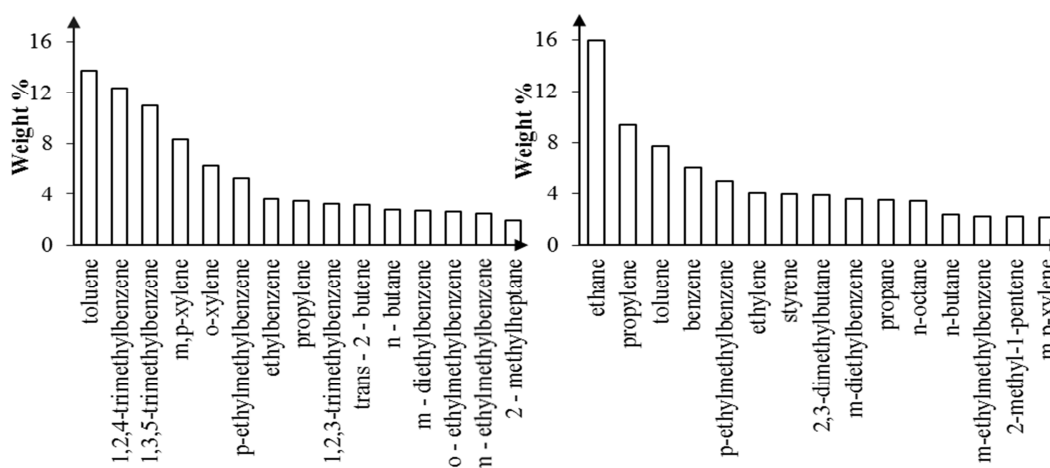

| *Figure 1.* Vehicular emission profile. | *Figure 2.* Biomass burning emission profile. |

Profiles of four other potential VOC sources that were selected and calculated from the literature review, as below:

3.2.1. Gasoline evaporation

Gasoline evaporation profile was calculated based on the data in the research of Imamura *et al.*, 2006 about VOC contents in gasoline at Ha Noi, Viet Nam [12]. This is the only literature available about gasoline evaporation in Ha Noi. This profile, however, can be slightly different from the gasoline evaporation profile at the investigated time of this research. In the study of Imamura, there were four types of gasoline (RON 83, RON 90, RON 92 and RON 95) available; however, in the current study, only RON 92 and RON 95 plus a small amount of ethanol blended gasoline E5 RON 92 (9 %) were used [13].

3.2.2. Industrial production

There are some industrial zones housing leather and shoes, rubber, soap, tobacco, optical glass, footwear, printing, and textile companies located in inner and vicinity areas of Hanoi. Industrial sources were predicted to contribute on VOCs levels. Industrial emission profile which was taken at industrial zone that consists of chemical industries, iron and steel plants, and cogeneration power in China was chosen to apply in this study. Toluene was the main compound in this profile. Toluene was considered as a major component which emits from activities such

as chemical production, the manufacture of adhesive products, *etc.* [14] and widely considered as main components of VOCs emission from industry.

3.2.3. Cooking

Cooking fume is regarded as one of the main sources of urban atmospheric VOCs. Chemical characteristics of cooking fume depend on cooking style and used fuels. Cooking emission profile was selected from Wang *et al.* 2018 [15] because of the similarities in cooking style, stove scale as family kitchen and used fuel (liquefied petroleum gas) to those in Ha Noi.

3.2.4. Paint

Before observation time, some buildings nearby the sampling sites were painted. Water-based paint was used. The water-based paint emission profile was extracted from the research of Liu *et al.* [11].

Table 1. Source profiles applied in the CMB calculation (unit: wt%).

Volatile organic compounds	Traffic*		Biomass*		Gasoline eva.		Paint		Cooking		Industry	
	Mean	*Unc*	*Mean*	*Unc*	*Mean*	*Unc*	*Mean*	*Unc*	*Mean*	*Unc*	*Mean*	*Unc*
Ethane	0.00	0.00	15.97	2.29	0.00	0.00	0.00	0.00	4.14	0.19	0.00	0.00
Propane	0.00	0.00	3.53	0.40	0.00	0.00	0.00	0.00	0.97	0.07	8.98	8.98
Propylene	3.46	0.96	9.40	2.71	7.12	7.12	0.00	0.00	1.45	0.28	0.00	0.00
n-butane	2.79	1.48	2.37	1.39	3.23	3.23	0.00	0.00	0.78	0.41	3.59	3.59
Trans-2-butene	3.13	1.11	2.05	0.29	4.07	4.07	0.00	0.00	0.12	0.00	0.00	0.00
2-methylhexane	0.67	0.23	0.32	0.56	7.23	7.23	0.00	0.00	5.79	0.14	0.00	0.00
2,2,4-trimethylpentane	1.30	0.31	0.60	0.13	0.00	0.00	0.00	0.00	21.73	0.53	0.00	0.00
Isopentane	0.94	0.33	0.21	0.36	20.50	20.50	0.00	0.00	0.33	0.04	0.00	0.00
2–methylpentane	0.14	0.20	1.00	1.12	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Toluene	13.74	1.56	7.77	0.61	12.98	12.98	19.00	19.00	1.29	0.11	70.66	70.66
Benzene	1.57	0.33	6.05	1.19	2.01	2.01	7.00	7.00	0.64	0.02	5.99	5.99
m,p-xylene	8.34	0.45	2.15	0.13	3.09	3.09	13.00	13.00	0.31	0.03	0.00	0.00
o-xylene	6.29	0.20	1.15	1.07	1.23	1.23	0.00	0.00	0.19	0.02	0.00	0.00
Ethylbenzene	3.59	0.68	1.38	0.15	0.00	0.00	0.00	0.00	0.40	0.04	5.99	5.99

*Note: * Source profiles that were developed in this study by monitoring;*
    Unc: Uncertainty.

3.3. Source apportionment

The receptor concentrations and the source profiles, with appropriate uncertainty estimates, serve as input data to CMB. In this study, receptor data consist of the average concentrations of

VOC species in ambient samples at 6 pm and the uncertainties were the standard deviation of those (in ppbC). Individual source profiles are formed from individual samples, thus they included mean and uncertainties in fraction (%) of all samples. In other words, mean mass fraction was an average of mass fraction that each VOC concentration normalized to all the compounds in individual samples. The uncertainties were then simply determined as the standard deviation of these average. Vehicular and biomass burning emission profiles were calculated using to this approach. Cooking profile uncertainties were chosen as standard deviation provided by supplement data from Wang *et al.* [15]. Regarding the remaining source profiles, a nominal uncertainty of 100 % was applied to the mean weight fractions because there were no further available information. US-EPA criteria for CMB model were fully met for the obtained results with $R^2 = 0.91$, $\chi^2 = 0.61$, and *%*mass = 86.1.

Figure 3 shows the source apportionment of VOCs. Vehicular emission contributed 37 %, made the most significant contribution to ambient VOCs; followed by biomass burning (21 %) and gasoline evaporation (20 %). Approximately 15 % of total ambient VOCs were attributed by industrial production whereas cooking and paint accounted for 5 % and 2. These results are consistent with previous researches by Truc and Kim Oanh [16] and Sakamoto *et al.* [2] saying that the major local emission source for VOCs was traffic, *e.g.* motorcycles. Gasoline evaporation was also identified as the significant contributor to the ambient VOCs, *e.g.* benzene level [12, 17]. Biomass burning was considered as the main VOCs source in Southeast Asia [6]. The result was reasonable because sampling time was at the lagging period of biomass burning occurring surrounded Ha Noi area.
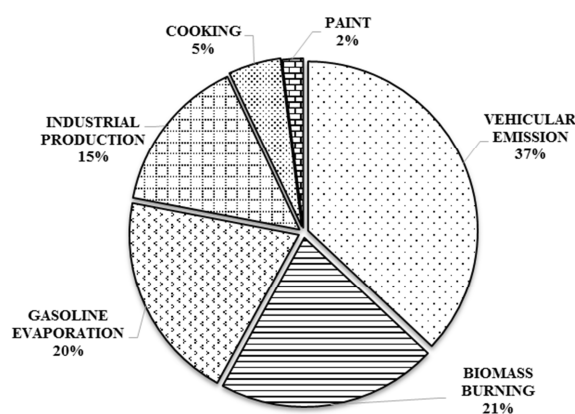

Figure 3. Source contribution resolved from CMB in Ha Noi.

4. CONCLUSIONS

In this study, ambient VOCs concentration and two emission profiles have been determined. In vehicular emission profile, toluene was the most abundant species of 13 %, followed by 1,2,4-trimethylbenzen, p,m-xylene, o-xylene of 11 %, 8 % and 6 %, respectively. In biomass burning emission profile, ethane and propylene accounted for the largest part of 16 % and 9 %, respectively.

CMB receptor model was used to analyze the sources of VOCs in Hanoi for the first time. The result showed that the main contributors were vehicle exhaust, biomass burning and gasoline evaporation of 37 %, 21 % and 20 % respectively. Industrial production accounted for 15 % whereas cooking and paint contributed 5 % and 2 %, respectively. These suggested that

effectively controlling vehicular exhaust such as improving vehicle technology and fuel quality are very important in Hanoi to control VOCs.

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