CHAPTER 1

INTRODUCTION

1.1 Rationale

Volatile Organic Compounds (VOCs)* are important precursors in photochemical reactions, secondary aerosol formation and are also hazardous to human health. As precursors in photochemical reactions, they cause an elevated tropospheric ozone level in urban areas. This ozone is harmful to human health, environment and our property. In regards to human health, it irritates eyes, and affects lung function. On environment, it affects plants and trees and reduces visibility. With regard to property, it affects the molecular structure of rubber and fabric causing a shortened working life.

From annual reports of the Pollution Control Department of Thailand (PCD) the maximum 1-hr ozone concentration in Bangkok from 1996 - 2004 frequently exceeded the National Ambient Air Quality Standard (Table 1.1).

The study "Investigation and Analysis of Ozone Precursors for the Mitigation of Photochemical Air Pollution in Bangkok" (PCD, 2001) found that if there were no additional measures on controlling ozone precursors, the maximum ozone concentration would increase to 203 ppb in 2005 and to 287 ppb in 2010. The National Ambient Air Quality Standard is 100 ppb.

In order to control ozone concentration, the sources of precursors need to be defined. Although ozone precursors are both NO_2 and VOCs, the previously mentioned PCD study concluded that ozone episodes in Bangkok are VOC-limiting.

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* VOCs in this study refer to gaseous aliphatic and aromatic non-methane hydrocarbons, C2 to C10, that have a vapor pressure greater than 0.14 mm. Hg at 25 °C.

Table 1.1 Ozone Concentration in Bangkok 1996 - 2004

Year	Maximum Hourly Ozone Concentration (ppb)
1996	324
1997	423
1998	191
1999	257
2000	203
2001	183
2002	162
2003	169
2004	173
National Ambient Air Quality Standard for 1-hr ozone concentration	**100**

Source: Summarized from Pollution Situation in Thailand, the annual report of the PCD for the years 1996 - 2004

VOCs are emitted from various anthropogenic and biogenic sources. In urban areas, VOCs are mainly from anthropogenic sources such as vehicle tailpipes emitting gases from both the complete and incomplete combustion of gasoline, evaporation of gasoline from engines and tanks, solvents used in industry as well as in household products (Watson, Chow, and Fujita, 2001). The Bangkok emission inventory by the PCD showed that 95% of VOCs are sourced from vehicles (PCD, 2001). That calculation was based on the combustion of fuel and evaporation from gas stations, excluding the solvent usages which scatter over the whole area of Bangkok such as usage of solvent-containing products. Data on solvent usage were not available in the PCD's emission inventory. However, VOC emission database of Bangkok in 2000 (Pongprueksa, 2001) showed that around 60% of VOCs are from vehicles and around 40% are from area sources such as refueling stations and the usage of solvent-containing products.

In emission inventory calculations, uncertainties for VOCs are greater than the criteria air pollutants such as TSP, SO_2, and NO_2 (Scheff and Wadden,1993). The diversity of VOC sources includes vehicles, industry, solvent-containing products, and biological processes. An estimation of volatilization is very difficult due to uncertainties in estimating solvent usage, temperature, and manner of application. Therefore, this study proposed to apply the receptor model, U.S. EPA Chemical Mass Balance (CMB7), to find out the source apportionment of VOCs in Bangkok ambient air.

1.2 Objectives

The objectives of this study are as follows:

1. Determine VOC concentrations in Bangkok ambient air
2. Speciation of VOCs in ambient air
3. Determine source profiles of various sources of VOCs
4. Use a modified receptor model to determine source apportionment of VOCs in Bangkok ambient air

1.3 Hypothesis

The contribution of VOCs from various sources at a receptor can be derived from the proportion of VOCs at the receptor and at the emission sources.

Principle of the Receptor Model

The Receptor model is a statistical model used to identify the contributions of sources to receptors. This model requires input data such as the concentration of VOCs at a receptor (ambient), and the composition of VOCs from emission sources. Source contribution is calculated by weighted least-square multiple regression analysis. An equation is shown as follows (U.S. EPA., 1990):

$$C_i = F_{i1} S_1 + F_{i2} S_2 + \ldots + F_{ij} S_j + \ldots\ldots + F_{iJ} S_J + E \qquad i = 1 \ldots\ldots I \,,\, j = 1 \ldots\ldots J$$

Where: C_i = Concentration of VOC species i measured at a receptor site

F_{ij} = Fraction of VOC species i in emissions from source j

S_j = Estimation of the contribution of source j

I = Number of VOC species ($I \geq J$)

J = Number of source types

E = Uncertainty

Source contribution estimations; Sj, are the main output of the model. To show the goodness of fit of modeling calculations, the model uses Sj to calculate Ci and compares the calculated Ci to the measured Ci and also calculates the other parameters: R^2, Chi-square, TSTAT, and the percent mass.

Target VOC species in this study

Target VOC species in this study (Table 1.2) refers to the VOCs listed in Technical Assistance Document for Sampling and Analysis of Ozone Precursors (U.S. EPA, 1998). These VOCs were selected based on their abundance in urban atmospheres and their potential role in the formation of ozone.

Table 1.2 Target Volatile Organic Compounds

No.	Name	No.	Name
1.	Ethylene	2.	Acetylene
3.	Ethane	4.	Propylene
5.	Propane	6.	Isobutane
7.	1-Butene	8.	*n*-Butane
9.	*trans*-2-Butene	10.	*cis*-2-Butene
11.	Isopentane	12.	1-Pentene
13.	*n*-Pentane	14.	Isoprene (2-methyl-1,3-butadiene)
15.	*trans*-2-Pentene	16.	*cis*-2-Pentene
17.	2,2-Dimethylbutane	18.	Cyclopentane
19.	2,3-Dimethylbutane	20.	2-Methylpentane

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Table 1.2 (Con't)

No.	**Name**	**No.**	**Name**
21.	3-Methylpentane	22.	*n*-Hexane
23.	Methylcyclopentane	24.	2,4-Dimethylpentane
25.	Benzene	26.	Cyclohexane
27.	2-Methylhexane	28.	2,3-Dimethylpentane
29.	3-Methylhexane	30.	2,2,4-Trimethylpentane (isooctane)
31.	*n*-Heptane	32.	Methylcyclohexane
33.	2,3,4-Trimethylpentane	34.	Toluene
35.	2-Methylheptane	36.	3-Methylheptane
37.	*n*-Octane	38.	Ethylbenzene
39.	*m/p*-Xylene	40.	Styrene
41.	*o*-Xylene	42.	*n*-Nonane
43.	Isopropylbenzene (cumene)	44.	*n*-Propylbenzene
45.	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)	46.	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
47.	1,3,5-Trimethylbenzene	48.	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
49.	1,2,4-Trimethylbenzene	50.	*n*-Decane
51.	1,2,3-Trimethylbenzene	52.	*m*-Diethylbenzene
53.	*p*-Diethylbenzene	54.	*n*-Undecane

Source: U.S. EPA, 1998

1.4 Expected Outcomes

1. VOC species from ambient air in Bangkok are determined.
2. VOC emission source profiles of selected sources such as gasoline vehicles, diesel vehicles, gasoline vapor, solvent-based paint, food barbequing, biomass burning, and municipal waste disposal are analyzed.
3. The receptor model, U.S. EPA CMB7, is applied to find out contributions of the various sources of VOCs to receptors.
4. Validation of existing emission inventory concerning major VOC sources.
5. The VOC control strategies for Bangkok air quality management can be derived based on the results from the receptor model.