CHAPTER 2

LITERATURE REVIEW

2.1 Ozone Formation and Its Precursors

Ozone episodes is one of the air pollution problems in Bangkok. The results from the ambient air monitoring stations showed that ozone concentrations sometimes exceeded the National Ambient Air Quality standard. The study "Investigation and Analysis of Ozone Precursors for the Mitigation of Photochemical Air Pollution in Bangkok" concluded that the ozone concentration in the dry season (November to March) was higher than in the rainy season (April to September) because the rainy season is often cloudy, but in dry season there is strong sunlight (PCD, 2001) which favored ozone formation.

2.1.1 Ozone Formation

Ozone occurs from the photochemical reaction of nitrogen dioxide (NO_2) and Volatile Organic Compounds (VOCs) in the presence of sunlight. Table 2.1 shows a simplified photochemical reaction leading to ozone formation in ambient air. Reactions (a) and (b) are recycling reactions. However, in an urban atmosphere with a variety of VOCs, reactions (c) and (d) promote the production of peroxy radical (RO_2). Increasing amounts of RO_2 lead to increasing amounts of NO_2 in ambient air by reaction (e). Increasing amounts of NO_2 lead to increasing levels of O_3 by reactions (a) and (b).

Table 2.1   Simplified Photochemical Reaction

(a) O_3 Production	$NO_2 + hv \longrightarrow NO + O$
	$O + O_2 + M \longrightarrow O_3 + M$
(b) NO and O_3 recycling	$NO + O_3 \longrightarrow NO_2 + O_2$
(c) Radical Production	$O_3 + hv \longrightarrow O(^1D) + O_2$
	$O(^1D) + H_2O \longrightarrow 2OH$
(d) Hydrocarbon loss	$OH + RH \longrightarrow R^\bullet + H_2O$
	$R^\bullet + O_2 \longrightarrow RO_2$
(e) NO $\longrightarrow$ NO_2 oxidation	$RO_2 + NO \longrightarrow RO + NO_2$
	$CO + OH + O_2 \longrightarrow CO_2 + HO_2$
	$HO_2 + NO \longrightarrow NO_2 + OH$

Source: Weeks, et al., 2001

2.1.2 Ozone Precursors

As mentioned above, ozone occurs as a result of a photochemical reaction of NO_2 and VOCs in the presence of sunlight.

NO_2 is an air pollutant emitted from the combustion of fossil fuel. Anthropogenic sources of NO_2 are vehicles and combustion facilities such as power stations. An NO_2 emission inventory can be calculated by emission factors for each source activity.

VOCs are variety of compounds with different physical and chemical properties. These are not only pure hydrogen and carbon containing compounds (hydrocarbons) but also compounds containing oxygen, chlorine and other elements. Anthropogenic sources of VOCs are: 1) combustion processes especially internal combustion, 2) processing, storage and distribution of fossil fuel, 3) the application of volatile organic solvents and solvent containing products such as paint and varnish, 4) industrial production processes, and 5) biological processes, both bacterial activity and higher plant activity (Friedrich and Obermeier, 1999). Higher plants emit VOCs including for example, deciduous trees and shrubs which emit isoprene and conifers which emit pinene and limonene (Baird, 1999).

The reactivity of each VOC species is measured by a reaction coefficient of each species with hydroxyl radical (OH) at 298 K. 1 atm (Atkinson, 1990). A lifetime in ambient air of those target VOC species in this study (Appendix A) were calculated by comparing to trichloroethane (CH_3CCl_3) whose lifetime is 5.7 years, and reaction coefficient, K_{OH}, with OH radical is 0.01 x 10 $^{-12}$ cm^3/molecule/sec at 298 K 1 atm. (Seinfeld, 1999). Table 2.2 shows the urban VOC species found in some cities (Weeks, et al., 2001).

Table 2.2   Ambient VOC Concentrations Observed in Some Cities

VOCs	Concentration, ppbC			
	39 USA Cities		Sydney	Melbourne
	Median	Maximum	Average	Peak Hour
Ethylene	21.4	1001	25.0	64.7
Acetylene	12.9	114	20.2	48.1
Ethane	23.3	475	15.0	29.6
Propylene	7.7	455	22.2	27.1
Propane	23.5	393	17.7	61.1
Isobutane	14.8	1433	18.8	37.7
1-Butene	5.9	365	4.0	5.6
n-Butane	40.3	5448	30.0	62.6
trans-2-Butene			4.4	4.5
cis-2-Butene			4.0	3.8
Isopentane	45.3	3393	45.0	62.9
1-Pentene			2.0	3.1
n-Pentane	22.0	1450	25.0	34.6
trans-2-Pentene			3.0	3.6
cis-2-Pentene			3.5	
2,2-Dimethylbutane			3.0	
Cyclopentane			3.5	2.2
2,3-Dimethylbutane			5.4	
2-Methylpentane	14.9	647	15.6	22.0
3-Methylpentane	10.7	351	9.6	14.9
n-Hexane	11.0	601	12.6	17.1

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Table 2.2   (Con't)

VOCs	Concentration, ppbC			
	39 USA Cities		Sydney	Melbourne
	Median	Maximum	Average	Peak Hour
Methylcyclopentane	6.4	293	7.2	
Benzene	12.6	273	15.6	47.4
2-Methylhexane	7.3	173	8.4	
3-Methylhexane	5.9	168	5.6	
2,2,4-Trimethylpentane	6.8	106		5.8
n-Heptane	4.7	233		6.0
Toluene	33.8	1299	62.3	90.9
n-Octane			3.2	2.5
Ethylbenzene	5.9	159	10.4	12.3
m/p-Xylene	18.1	338	31.2	47.9
o-Xylene	7.2	79	12.0	17.3
n-Nonane			3.6	2.7
n-Propylbenzene			3.6	
m/p-Ethyltoluene	5.3	83	9.9	
1,3,5-Trimethylbenzene			4.5	12.4
o-Ethyltoluene			3.6	
1,2,4-Trimethylbenzene	10.6	81	11.7	13.0
n-Decane			5.0	2.3

Source: Weeks et al., 2001

▓ Not applicable

2.2   Volatile Organic Compound Concentration in Ambient Air

The Pollution Control Department (PCD) has 14 ambient air monitoring stations in Bangkok. Air pollutants being monitored are criteria air pollutants such as TSP, PM10, SO_2, NO_2 and O_3. At some stations hydrocarbons are monitored in terms of total hydrocarbon, methane and non-methane hydrocarbon (NMHC). Data of non-methane hydrocarbon during August 1996 to November 1999 showed the average 1-hr concentration at around 0.2 - 2.3 ppm (PCD, 2001).

The average NMHC observed in background air and roadway air in Bangkok in 2000 were around 0.568 ± 0.230 ppmC, and 4.176 ± 1.502 ppmC, respectively (Limpaseni, et al., 2003). Table 2.3 compares the average NMHC concentration observed in Melbourne, Hong Kong, and Bangkok.

Table 2.3   Average Total Non-methane Hydrocarbon Concentration Observed in Some Cities

Unit: ppmC

City	Background	Roadway
Melbourne	0.242 ± 0.158 (21)	0.980 ± 0.070 (19)
Hong Kong	0.229 ± 0.058 (6)	0.616 ± 0.232 (34)
Bangkok	0.568 ± 0.230 (11)	4.176 ± 1.502 (11)

In brackets are numbers of samples

Source: Limpaseni et al., 2003

Laowakul, et al. (2003) reported total identified VOCs (TVOC) in Bangkok ambient air at around $1,036.5 - 5,379.1$ $\mu g/m^3$. Besides the concentration of TVOC, they also reported the ratio of benzene to toluene in Bangkok ambient air of around $0.2 - 0.4$. The benzene to toluene ratio is used to indicate the VOCs from vehicles. The previous study of Scheff and Wadden (1993) suggests that the benzene to toluene ratio from vehicles is around 0.5.

From the health aspect, benzene is considered to be a carcinogen. Laowakul, et al. (2003) showed the benzene concentration in Bangkok ambient air to be $73.9 - 244.9$ $\mu g/m^3$. From the guidelines of WHO, the concentration of airborne benzene associated with an excess lifetime risk of $1/10^4$, $1/10^5$ and $1/10^6$ are 17, 1.7 and 0.17 $\mu g/m^3$, respectively (WHO, 2000).

2.3   Emission Inventory of VOCs

The first emission inventory of air pollutants in Bangkok was done in 1992. The air pollutants; TSP, SO_2, NOx, CO and HC (or VOCs) were calculated from fuel consumption in industrial sources, traffic sources and area sources in Bangkok Metropolitan Region (BMR), Bangkok, Samut Prakan, Nonthaburi, Pathum Thani, Nakhon Pathom, and Samut Sakhon (PCD, 1994). The results of this study showed that 14% of HC (or VOCs) were from power plants, 27 % were from industrial sources, 55% were from traffic sources, and 4% were from commercial and residential sources.

In 1997 the Bangkok emission inventory was updated (PCD, 2001). The results based on combustion of fuel showed that 95% of VOCs were from vehicles, 4.7% from area sources (mainly from fuel evaporation at gas stations) and 0.2% from industrial sources. The data excluded the usage of solvent containing products which are scattered over the whole area of Bangkok. Data on solvent use was not included in PCD's emission inventory. Pongpreuksa (2001) conducted a VOC emission database of Bangkok in 2000 which showed that 60% of VOCs were from vehicles and 40% were from area sources consisting of 37% from paint and thinner use and 3% from refueling.

In Europe, road transport is the largest anthropogenic source of VOC emissions and solvent use is the second largest anthropogenic source of VOCs, especially the use of paint and varnish in various sectors such as industry, car manufacturing, construction and building, and domestic use (Reis and Friedrich, 2000). Table 2.4 is the emission inventories of VOCs from various sources in Bangkok and 15 countries in the EU.

Table 2.4   Emission Inventories of VOCs in Bangkok and the EU

Unit %

Item	Sources	Bangkok 1992 (a)	Bangkok 1997 (b)	Bangkok 2000 (c)	The EU 15 countries (d)
1	Road transport	55	95.1	60	31
2	Solvent use			37	27
3	Nature				
4	Waste treatment and disposal				7
5	Production Processes				6
6	Extraction and Distribution of fossil fuels				6
7	Other mobiles sources and machinery				5
8	Agriculture				4
9	Commercial, Institutional and residential combustion	4			4
10	Public Power, Co-generation and district heating	14			1
11	Industrial combustion	27	0.2	0	0.4
12	Vapor of gasoline/refueling		4.7	3	

Sources: (a) PCD, 1994

(b) PCD, 2001

(c) Pongpreuksa, 2001

(d) Reis, and Friedrich, 2000

▨ not applicable

2.4   Receptor Model

In air quality modeling there are two different types of models: (1) the source-based model, and (2) the receptor-based model. The source-based model needs emission data and meteorological data including chemical reaction for reactive air pollutants as input data to calculate <u>concentration of air pollutants in ambient air</u>. The precision of result depends on the availability and accuracy of emission data, good records of meteorological data, and also a thorough understanding of chemical reactions of air pollutants. The receptor-based model uses concentrations of various chemical species found at receptors and the fraction of these chemical species from various emission

sources to determine the <u>contribution of each type of emission source</u> to the ambient concentration at receptors.

The two methods of the mathematical receptor model which have been most widely used are the chemical mass balance method and the factor analysis method. The data at receptors can be screened using a classical factor analysis. The results of this type of model will show the major sources affecting receptors but need data from literature to compare what these sources should be. Factor analysis usually requires 40 data samples or more (Hopke, 1985).

For Bangkok where major sources are known, the chemical mass balance model (CMB) can be used. The CMB analysis is performed on one sample at a time so one ambient sample is the minimum sample number required. However, to achieve greater confidence in the conclusion regarding major sources, more samples are needed (Hopke, 1985).

Chemical Mass Balance (CMB) Receptor Model

The CMB Receptor Model is a statistical model applied to find out source contributions of pollutants which are transported from sources to receptors. Its basic concept is the use of chemical mass balance (Hopke, 1985). For example; it is assumed that the total compound C concentration measured at a receptor is a linear sum of compound C contributed from independent source types such as vehicles, solvent containing products, biomass burning, and so on.

CMB was firstly applied to investigate source apportionment of TSP and PM10 air pollutants. In 1981, the receptor model was applied to study source apportionment of VOCs in Tokyo (Wadden, et al., 1986) and after that there were many studies in many states in USA as shown in Table 2.5.

Table 2.5   Source Apportionment of VOCs in Selected Cities from Previous Studies

Sources	Source contribution by CMB (%)					
	Tokyo (1)	Illinois (2)	Chicago (3, 4)	Los Angeles (5)	California and San Francisco (6)	Bangkok (7)
Vehicles	7.0	60.8	21-35		35-70	33-88
Gasoline engine exhaust				31-37		
Whole liquid gasoline				32-38		
Headspace gasoline vapor				5-13		
Gasoline vapor	10.5	11.1	5-7		10-40	0
Petroleum refinery	26.5	10.1	7-11		30-50	0
Fuel oil boiler						0-46
Paint solvent	27.2				1-20	0
Architectural coating			2-3			
Graphic arts			1-6			0
Vapor degreasing			1-3	5-12		
Dry cleaning			0.3-0.4	0.14		
Biological processes/ Waste Treatment				10-15	10-15	
Biomass burning						12-61
Unexplained sources	29.3	17.9			2-20	0

Source: (1) Wadden, Tsushi, and Shinji, 1986

(2) O'shea, and Scheff, 1988

(3) Aronian, Scheff, and Wadden, 1989

(4) Scheff, and Wadden, 1993

(5) Harly, Hannigan, and Cass, 1992

(6) Fujita, et al.,1995

(7) Suwattiga, and Limpaseni, 2003

▨ not applicable

CMB is useful in air quality assessment. It is the direct apportionment of ambient concentration to their sources that is useful in developing control strategies. CMB can be used as the primary analysis tool in areas with poorly quantified emission rates for fugitive sources such as smoke and evaporation, etc (Watson et al., 2001).

Although a standard assumption on the CMB receptor model is that the composition of emission is preserved as an air mass moves from sources to receptors, the CMB receptor model can still be used in source apportionment of VOCs. There are studies supporting the use of the CMB in finding out source apportionment of VOCs. Wadden, Tsushi, and Shinji (1986) who compared the CMB modeling results of samples collected late in the day and early in the morning, and Scheff and Klevs (1987) who compared results from a model with 18 relatively well-matched VOCs and results when six highly reactive VOCs were added. Both studies found little difference in the estimation of source contributions, but found a poor agreement between predicted and observed concentrations of highly reactive VOCs. It was recommended that VOC samples should be collected in the morning to minimize the extent of reaction that could occur between source and receptor locations and should have a lifetime of more than 4 hours. Scheff and Wadden (1991, 1993) concluded that with relatively unreactive VOCs and source-to-receptor transport times of 1-4 hours, VOC fractionation did not significantly affect estimation of source apportionment. Therefore VOC fitting species used in this study are VOCs which have lifetime of more than 4 hours (Appendix A) and sampling times were from 8.00-12.00 am.

This study used the U.S. EPA CMB7 package, which gives an effective-variance weighted least square solution (U.S. EPA, 1990). The equation is as follows:

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

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

Sj is calculated by the model. After that the model uses Sj to calculate the parameters, which show the goodness of fit of the modeling calculations.

The parameters, which show the goodness of fit of the modeling calculations are as follows:

a) R^2 shows how well the source contribution estimates explain the measured concentration. The value of R^2 is between 0-1. The closer R^2 is to one, the better the source contribution estimates explain the measured concentration.

b) TSTAT is the ratio of the source contribution estimate to the standard deviation. The TSTAT value should be more than 2. TSTAT values which are less than 2 indicate that the sources contribution estimate is at or below a detection limit.

c) Chi-square is the weighted sum of the square of the differences between the calculated and the measured VOC species concentration. Chi-square equal to zero means there is no difference between calculated and measured VOC species concentration. Chi-square which is less than 1 means the calculated and measured fitting species are close together. The acceptable range is less than 2. Chi-square of more than 4 means the calculated value does not explain one or more measured VOC species.

d) Percent Mass is the percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration. The acceptable range is between 80-120%.