AN ESTIMATED BENZENE AND TOLUENE EXPOSURE MODEL OF GASOLINE SERVICE ATTDNDANTS

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Thesis

Entitled

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AN ESTIMATED BENZENE AND TOLUENE EXPOSURE MODEL OF GASOLINE SERVICE ATTENDANTS

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ABSTRACT

The aim of the study was to find a benzene exposure predicted model for gasoline station attendants. The subjects were 165 filling station attendants of 46 service stations belonging to three gasoline companies in Bangkok and boundary areas. A full-shift breathing zone air sampling of service attendants together with gasoline octane 91 and 95 was collected to determine benzene and toluene concentrations by gas chromatography. The environmental conditions namely, wind speed, temperature, relative humidity were collected every 40 min. at the stations. In addition, gasoline sold on the day of sample collection was also done. The relationship among several factors and atmospheric benzene and toluene concentrations were determined using Pearson correlation coefficient and Spearman rank correlation coefficient. A benzene and toluene exposure estimated model of gasoline station attendants using several variables was carried out using linear multiple regression analysis.

The result showed average benzene and toluene in breathing zone air of station attendants were 54.48 ± 30.16 and 78.63 ± 38.02 ppb, respectively, benzene concentrations in gasoline octane 91 and 95 were 1.69 ± 0.49% and 1.55 ± 0.41%, respectively; and toluene concentrations in gasoline octane 91 and 95 were 7.23 ± 2.47% and 7.01 ± 1.78 % respectively. The atmospheric benzene in the three brands studied were significantly different at p-value <0.05. The relationship of atmospheric benzene with other factors showed a significant difference for benzene concentration in gasoline octane 91 and 95 (p-value <0.05), and quantity of gasoline sold (p-value <0.05). The atmospheric toluene in the three brands studied were significantly different at p-value <0.05. The relationship of atmospheric toluene with other factors showed a significant difference for toluene concentration in gasoline octane 91 and 95 (p-value <0.05), and quantity of gasoline sold (p-value <0.05).

The result produced 2 appropriate models for estimation of atmospheric benzene exposure among service attendants as follows: Model I: $Y1 = -17.49 + 2.16X1 + 35.41X3$, with r^2 =0.512 and Model II: $Y1 = -23.07 + 2.58X1 + 35.82X3$, with r^2 =0.547, and 2 appropriate models for estimation of atmospheric toluene exposure among service attendants were as follows: Model III, $Y2 = -14.634 + 11.238Z2$, with $r^2 = 0.515$ and Model IV: $Y2 = -13.17 + 10.276Z2 + 2.43 \times 10^{-3}X1$, with $r^2 = 0.529$ where Y1 = atmospheric benzene concentration, Y2 = atmospheric toluene concentration, X1 = quantity of gasoline sold, X3 = benzene in gasoline 95 and Z2 = toluene in gasoline 95. All models can be used to estimate atmospheric benzene and toluene exposure among service attendants with at least 51.2% accuracy. The most influencing factor of atmospheric benzene concentration is quantity of benzene or toluene in gasoline. Therefore, reduction of quantity of benzene or toluene in gasoline should be implemented to reduce atmospheric benzene or toluene exposure in gasoline service attendants.

KEY WORDS : BENZENE / TOLUENE / GASOLINE

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รูปแบบการประมาณค่าการสัมผัสสารเบนซีนและโทลูอีนของพนักงานที่ให้บริการเติมน้ำมัน (AN ESTIMATED BENZENE AND TOLUENE EXPOSURE MODEL OF GASOLINE SERVICE ATTENDANTS)

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บทคัดย่อ

การศึกษาครั้งนี้มีวัตถุประสงค์เพื่อหารูปแบบการทำนายการได้รับสารเบนซีนจากไอน้ำมันเบนซิน (Gasoline) ในพนักงานที่ปฏิบัติงานในสถานีบริการน้ำมัน กลุ่มตัวอย่างเป็นพนักงานที่มีหน้าที่เติมน้ำมันให้รถยนต์ในสถานีบริการน้ำมันเชื้อเพลิง 46 แห่งในเขตกรุงเทพมหานครและปริมณฑล จำนวน 165 คน เก็บตัวอย่างความเข้มข้นของเบนซีและโทลูอีนที่ระดับลมหายใจของพนักงาน ตลอดระยะเวลาทำงาน 1 วัน และมีการเก็บตัวอย่างน้ำมันเบนซิน 91 และ 95 เพื่อวิเคราะห์หาปริมาณสารเบนซินด้วยเครื่องแก๊สโครมาโตกราฟ มีการตรวจวัดปัจจัยด้านสิ่งแวดล้อม ได้แก่ ความเร็วลม, อุณหภูมิ และความชื้นสัมพัทธ์ ทุกๆ 40 นาที ในบริเวณสถานีบริการน้ำมัน รวมทั้งเก็บข้อมูลยอดขายน้ำมันเบนซินที่ขายได้ในกะนั้น หลังจากนั้นวิเคราะห์หาความสัมพันธ์ระหว่างปัจจัยต่างๆ กับปริมาณความเข้มข้นของเบนซีนในอากาศ โดยใช้สถิติ Pearson correlation coefficient และ Spearman's rank correlation coefficient เพื่อนำหารูปแบบการทำนายของความสัมพันธ์ระหว่างตัวแปรต่างๆ โดยใช้การวิเคราะห์ linear multiple regression analysis

ผลการศึกษาพบว่าระดับความเข้มข้นเฉลี่ยของสารเบนซีนและโทลูอีนในอากาศที่บริเวณหายใจของพนักงานมีค่าเท่ากับ 54.48 ± 30.16 และ 78.63 ± 38.02 ppb ตามลำดับ ปริมาณเบนซีนในน้ำมันเบนซินออกเทน 91 และ 95 มีค่าเท่ากับ 1.69 ± 0.49% และ 1.55 ± 0.41% ตามลำดับ และปริมาณโทลูอีนในน้ำมันออกเทน 91 และออกเทน 95 มีค่าเท่ากับ 7.23 ±2.47% และ 7.01±1.78% ตามลำดับ ระดับความเข้มข้นเฉลี่ยของเบนซีนและโทลูอีนในอากาศในแต่ละสถานีบริการน้ำมันทั้ง 3 ยี่ห้อ พบความแตกต่างอย่างมีนัยสำคัญ (p-value <0.05) ส่วนความสัมพันธ์ของความเข้มข้นเฉลี่ยของเบนซีนในอากาศ กับปัจจัยอื่นๆที่พบว่ามีความสัมพันธ์อย่างมีนัยสำคัญอย่างน้อย 95% (p-value <0.05) ได้แก่ ปริมาณเบนซีนในน้ำมันเบนซินออกเทน 91 และ ออกเทน 95, และยอดขายน้ำมัน, ส่วนการหาความสัมพันธ์ของความเข้มข้นเฉลี่ยของโทลูอีนในอากาศกับปัจจัยอื่นๆ ที่พบว่ามีความสัมพันธ์อย่างมีนัยสำคัญ อย่างน้อย 95% (p-value <0.05) ได้แก่ ปริมาณโทลูอีนในน้ำมันเบนซินออกเทน 91 และ ออกเทน 95, และยอดขายน้ำมัน เมื่อนำปัจจัยที่มีความสัมพันธ์เหล่านี้ มาหารูปแบบการทำนายความสัมพันธ์เชิงเส้นตรงของความเข้มข้นของเบนซีนในอากาศได้ 2 รูปแบบ คือ $Y1 = -17.49 + 2.16X1 + 35.41X3$ (r^2 =0.512) และ $Y1 = -23.07 + 2.58X1 + 35.82X3$ (r^2 =0.547) ส่วนรูปแบบการทำนายความสัมพันธ์เชิงเส้นตรงของความเข้มข้นของโทลูอีนในอากาศได้ 2 รูปแบบ คือ $Y2 = -14.634 + 11.238Z2$ ($r^2 = 0.515$) และ $Y2 = -13.17 +10.276Z2 + 2.43x10^{-3}X1$, ($r^2 = 0.529$) โดย Y1 = ความเข้มข้นเบนซีนในอากาศ, Y2 = ความเข้มข้นโทลูอีนในอากาศ, X1 = ยอดขายน้ำมันเบนซิน, X3 = ปริมาณเบนซินในน้ำมันเบนซินออกเทน 95 and Z2 = ปริมาณโทลูอีนในน้ำมันเบนซินออกเทน 95 ซึ่งรูปแบบการทำนายความสัมพันธ์ทุกรูปแบบ มีค่าสัมประสิทธ์สหสัมพันธ์อย่างน้อย 0.512 โดยปัจจัยที่มีอิทธิพลมากที่สุด คือ ปริมาณเบนซินและโทลูอีนในน้ำมันเบนซิน ดังนั้น การลดปริมาณเบนซินและโทลูอีนในน้ำมันเบนซิน จะทำให้ปริมาณเบนซีนและโทลูอีนที่พนักงานเติมน้ำมันที่อาจรับสัมผัสเข้าไปลดลง

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CHAPTER I
INTRODUCTION

1.1 Introduction

The first national economic and social development plan of Thailand in 1961 caused continuously expanded economy until present. Industrial development, transportation and energy consumption have been growing together for a long time. A statistics from Department of Land Transport, Ministry of Communications in the year 1997-2001, showed that total yearly increase of automobile averaged 1,000,000 per year causing energy demand rapidly increased, especially in Bangkok and boundary area (1).

A well known energy is gasoline. From oil and Thailand 2001 report, it showed that total quantity of gasoline consumption was 7,000 million liter (3,000 million liters for gasoline 95 and 4,000 million liters for gasoline 91and 87). Forty percentage of gasoline was used in Bangkok and boundary area. The gasoline was used mainly in transport sector for 98% and the rest (2%) was used in other sectors (2).

Gasoline is a complex mixture of volatile hydrocarbons, predominantly in the C4-C12 range, with a boiling point range of 50-200 °C. Gasoline may contain benzene in the range of 0-7% and typically contain 2-5%. The benzene concentration in gasoline in Thailand is usually defined by government regulation. Benzene must not more than 3.5% and aromatic hydrocarbon must not more than 35% by volume (3). Since benzene is a volatile and aromatic hydrocarbon, exposure to benzene may cause health effects. Short-term exposure may have respiratory tract irritation, skin and eye irritation, dizziness, headache and narcotic. Exposure to high concentration of benzene (usually more than 1,000 ppm), shows signs of central nervous system disorders, giddiness, euphoria, nausea and headache. Long–term exposure to a high concentration of benzene induces hemopoietic toxicity and increases the risk of cancer

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because benzene has been identified as a human carcinogen or leukemia causing agent (4). While benzene exposure in the workplace is decreasing, petroleum containing a few percent of benzene has become an important source of benzene exposure (5). Benzene exposure in workplace and gasoline service stations should be stringently controlled to decrease exposure, mainly exposure of gasoline service station attendants.

Nowadays, there are some researches about benzene exposure in gasoline service station in many countries but it is a few in Thailand especially predicted model of benzene exposure in gasoline service station attendant. So, this research determines the level of benzene exposure, factors affected benzene exposure of service station attendants, and a trend of benzene exposure for workers in gasoline service station. It leads to planning benzene exposure prevention.

1.2 Objectives

1.2.1 The general objective:

To determine an estimated benzene and toluene exposure model of gasoline service station attendants.

1.2.2 The specific objectives:

2.2.1 To evaluate the benzene concentration in air of service station attendants' exposure.

2.2.2 To study the relationship between benzene concentration in working area and factors affecting benzene exposure of gasoline service station attendants.

2.2.3 To determine the benzene and toluene exposure predicted model of gasoline service station attendants.

1.3 Hypothesis

1.3.1 The quantity of benzene in gasoline has an effect on benzene exposure of gasoline service station attendants.

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1.3.2 The quantity of gasoline sold each day affected on benzene exposure of gasoline service station attendants.

1.3.3 The environmental factors i.e. wind speed, temperature and humidity have affected on benzene exposure of gasoline service station attendants.

1.4 Scope of study

This research will take air sample at gasoline service station in Bangkok and boundary area and analysis by gas chromatograph (GC) following NIOSH method number 1501.

1.5 Variables

1.5.1 Independent variables

1.5.1.1 The quantity of benzene in gasoline

1.5.1.2 Amount of gasoline sold each day

1.5.1.3 Environmental factors

- Wind speed
- Temperature
- Relative humidity

1.5.2 Dependent variables

- Benzene concentration in air of service station attendants

1.6 Glossary of terms and definitions

Gasoline: It is an unleaded gasoline fuel oil octane 91 and octane 95 which has been sold in gasoline service station.

Service station attendants: Worker in gasoline service station who filling gasoline oil for service cars.

The quantity of benzene in gasoline: The level of benzene which has been mixed in gasoline both for octane 91 and octane 95

The benzene concentration in air: The quantity of benzene which was measured in air sample at breathing zone of gasoline service station attendants.

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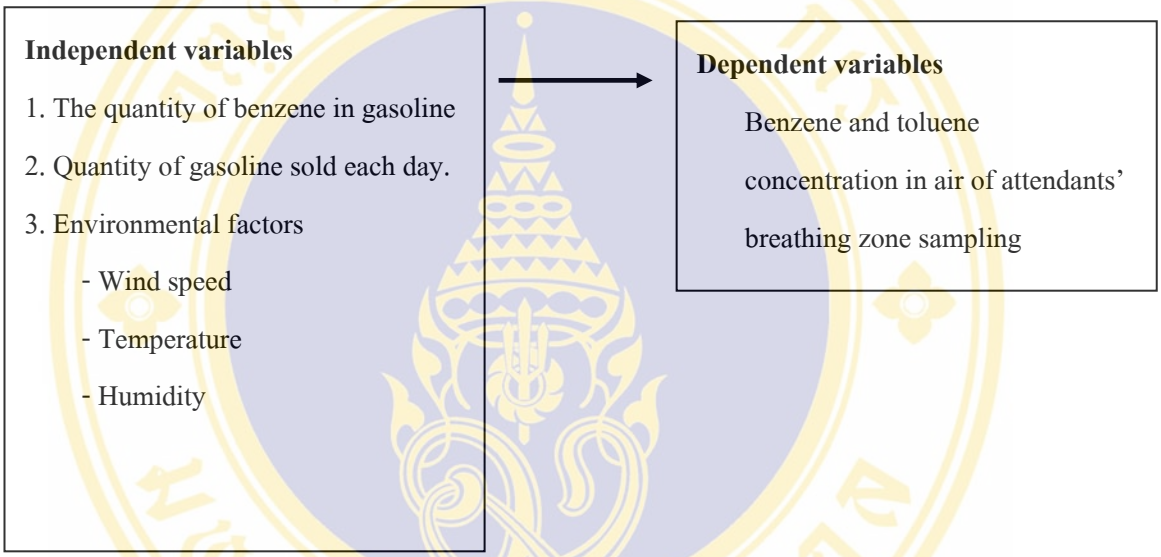
Amount of gasoline sold each day: The quantity of gasoline sold on the sampling day after the end of shift.

Wind speed: It is a wind speed in gasoline service station which was measured by wind speed instrument at breathing zone level of employee

1.7 Conceptual framework



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CHAPTER II
LITERATURE REVIEW

2.1 GASOLINE

2.1.1 General Information of Gasoline (6),(7)

Gasoline is produced from petroleum in the refining process which used as a fuel for engines in automobiles and other vehicles. It is a complex mixture of volatile organic hydrocarbons, predominantly in the C_4-C_{12} range, with a boiling point range of 50-200 ^{o}C (USA) or 25-220 ^{o}C (Europe). Most automotive gasoline is produced by blending naphtha process streams, such as light straight-run, reformed, alkylate, isomerization and thermally and catalytically cracked naphthas. Alkylated naphtha is typically the main component used in the production of aviation gasoline. Saleable gasoline may contain numerous additives, such as alkyl lead compounds, 1,2-dibromoethane (ethylene dibromide), 1, 2-dichloroethane (ethylene dichloride), alkyl phosphates, phenols, alcohols and methyl-*tert*-butyl ether, in order to meet product specifications. Automotive gasoline may contain 0-7%, and typically contain 2-3%, benzene (6). Typically, gasoline contains more than 150 chemicals including small amounts of benzene, toluene, xylene, and sometimes lead. How the gasoline is made determines which chemicals are present in the gasoline mixture and how much of each is presented. The actual composition varies with the source of the crude petroleum, the manufacturer, and the time period of year. Gasoline is a colorless, pale brown or pink liquid. Gasoline is very flammable; it catches on fire quite easily, evaporates quickly, and forms explosive mixtures with air (7).

The composition of hydrocarbon for typical automotive gasoline is shown in Table 1 (7)

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Table 1 The composition of hydrocarbon for gasoline

Component	Percentage Composition[b]	Component
n-alkanes		Other possible components
C_5	3.0	octane enhancers
C_6	11.6	methyl t-butyl ether (MTBE)
C_7	1.2	t-butyl alcohol (TBA)
C_9	0.7	ethanol
C_{10}-C_{13}	0.8	methanol
total of *n*-alkanes	17.3	antioxidants
		N,N'-dialkylphenylenediamines
branched alkanes		2,6-dialkyl and 2,4,6-trialkylphenols
C_4	2.2	butylated methyl, ethyl and dimethyl phenols
C_5	15.1	triethylene tetramine di(monononylphenolate)
C_6	8.0	metal deactivators
C_7	1.9	*N,N'*-disalicylidene-1.2-ethanediamine
C_8	1.8	*N,N'*-disalicylidene-propanediamine
C_9	2.1	*N,N'*-disalicylidene-cyclohexanediamine
C_{10}-C_{13}	1.0	disalicylidene-N-methyl-dipropylene-triamine
total of branched	32.0	ignition controllers
		tri-o-cresylphosphate (TOCP)
cycloalkanes		icing inhibitors
C_6	3.0	isopropyl alcohol
C_7	1.4	detergents/dispersants
C_8	0.6	alkylamine phosphates
total of cycloalkanes	5.0	poly-isobutene amines
		long chain alkyl phenols
olefins		long chain alcohols
C_6	1.8	long chain carboxylic acids
total of olefins	1.8	long chain amines
		corrosion inhibitors
aromarics		carboxylic acids
benzene	3.2	phosphoric acids
toluene	4.8	sulfonic acids
xylenes	6.6	
ethylbenzene	1.4	
C_3-benzenes	4.2	
C_4-benzenes	7.6	
others	2.7	
total aromatics	30.5	

[a]Adapted from Air Force 1989
[b]Percent by weight

2.1.2 Gasoline specification (3),(6)

The gasoline composition is varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline; hydrocarbons (wt %) is as follows: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; and 20-50% total aromatics (0.5-2.5% benzene) (6). Thai government regulation defines

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gasoline, where properties and test method are clearly defined. Thailand specification and test methods are listed in table 2 (3).

Table 2. Thailand specification and test method for gasoline (3)

Specification	Maximum rate	Minimum rate	Test method
1. Leaded content (g/l)	Not more than	0.013	ASTM D 3116 or equivalent
2. Sulfur content (%mass)	Not more than	0.10	ASTM D 4294
3. Phosphorus (g/l)	Not more than	0.0013	ASTM D 3231
4. Copper strip corrosion	Not more than	1	ASTM D 130
5. Oxidation stability, min	Not less than	360	ASTM D 525
6. Solvent washed gum	Not more than	0.004	ASTM D 381
7. Evaporated			ASTM D 86
10% Evaporated Temp, °C	Not more than	70	
50% Evaporated Temp, °C	Not more than,	110	
	Not less than	70	
90% Evaporated Temp, °C	Not more than	170	
End point, , °C	Not more than	200	
Residue, %vol	Not more than	2.0	
8. Vapor pressure at 37.8°C, KPA	Not more than	62	ASTM D 323 non oxygenate ASTM D 4953 oxygenate
9. Benzene (vol. %)	Not more than	3.5	ASTM D 3606
10. Aromatics (vol. %)	Not more than	35	ASTM D 4420
11. Water, %wt	Not more than	0.004	ASTM D 381
11.1 Non Oxygenate Blend		none	
11.2 Oxygenate Blend		0.7	ASTM E 203
12. Oxygenate compounds, vol.%	11	None	
13. PFI / IVDC additive			

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2.1.3 Physical and chemical properties of gasoline (7)

The physical and chemical properties of the gasoline mixture are shown in Table 3. In cases where data are not available for gasoline, ranges are given to indicate the different values for the individual components.

Table 3 Physical and chemical Properties of Gasoline

Property	Information	Reference
Molecular weight	108[a]	Anonymous 1989
Color	Colorless to pale brown or pink	Sax and Lewis 1989; Weiss 1986
Physical state	Liquid	Sax and Lewis 1989
Melting point	No data	
Boiling point	Initially, 39°C After 10% distilled, 60°C After 50% distilled, 110°C After 90% distilled, 170°C Final boiling point, 204°C	Budavari et al. 1989; OHM/TADS 1991; Sax and Lewis 1989
Density	0.7-0.8 g/cm^3[b]	IARC 1989
Odor	Gasoline odor	Weiss 1986
Odor threshold	0.025 ppm[c]	Weiss 1986
Solubility:		
Water at 20°C	Insoluble	OHM/TADS 1991; Sax and Lewis 1989
Organic solvent(s)	Absolute alcohol, ether, chloroform, benzene	Budavari et al. 1989; Sax and Lewis 1989
Partition coefficients:		
Log K_{ow}	2.13-4.87[d]	Air Force 1989
Log K_{oc}	1.81-4.56[d]	Air Force 1989
Vapor pressure[e]		ASTM 1989
at 60°C	465 mmHg	
at 56°C	518 mmHg	
at 51°C	593 mmHg	
at 47°C	698 mmHg	
at 41°C	773 mmHg	
Henry's law constant:		
at 20°C	4.8x10^{-4}-3.3 m^3/mol[d]	Air Force 1989
Autoignition temperature	280-486°C	NEPA 1986; Sax and Lewis 1989; Weiss 1986
Flashpoint	-46°C	Sax and Lewis 1989
Flammability limits	1.4-7.4%	Weiss 1986
Conversion factors	No data	
Explosive limits	1.3-6.0%	Budavari et al. 1989; Sax and Lewis 1989

[a]Average molecular weight
[b]Temperature not specified
[c]Not specified whether data for air or water
[d]Since data are not available for gasoline, ranges are given indicating different values for the individual components.
[e]The American Society for Testing and Materials (ASTM) has established guidelines on compositions of gasoline that will permit satisfactory performance under varying conditions. These guidelines define five volatility classes that vary by seasonal climatic changes. The values given for vapor pressure at the given temperatures are based on these volatility classes.

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2.1.4 General Population and Occupational Exposure (6),(7)

Occupational exposure to gasoline vapors occurs during production in petroleum refineries and during transport and distribution to retailers. Exposures to vapors are in most cases principally to lighter hydrocarbons, C_6 or lower. Personal 8-hr time-weighted average exposures of bulk and drum gasoline loaders and tank cleaners have been reported as 40-850 mg/m^3 total hydrocarbons and 1-27 mg/m^3 benzene, and for bulk loaders up to 6 mg/m^3 1,3-butadiene. Higher levels of benzene exposure have been reported for gasoline rail-loading and for some gasoline storage tank cleaning operations. Service station attendants and customers are exposed to lower levels of gasoline vapors.

Most people can begin to smell gasoline at 0.25 parts of gasoline per million parts of air (ppm) (7). The most likely way that you might expose to gasoline is by breathing its vapors at a service station when you are filling your car's fuel tank. If an attendant fills your car's fuel tank, you may still be exposed to vapors, but not as much as when you fill it yourself. If the hose from the gas tank leaks or you overfill your tank, you may be exposed to more gasoline vapors or some gasoline may spill on your skin. If you work at a service station, you will be exposed to more gasoline and its vapors than someone who just fills the car up occasionally.

Certain workers have a greater risk of exposure to gasoline vapors. These include service station attendants, drivers of gasoline tank trucks, workers at bulk loading terminals and marine loading docks, workers who remove and service underground storage tanks and gasoline pipelines, workers who find and clean up gasoline spills and leaks, and refinery workers. If you have any of these jobs, you are probably exposed to small amounts of gasoline vapors every day you work. If you work at a job using gasoline-powered equipment or vehicles, you may expose to gasoline and its vapors.

2.1.5 Health Effect (6)

Many of the harmful effects seen after exposure to gasoline are due to the individual chemicals in the gasoline mixture, such as benzene and lead in very small amounts. Inhaling or swallowing large amounts of gasoline can cause death. The levels of gasoline that killed people are about 10,000-20,000 ppm in air when breathed

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in and about 12 ounces when swallowed. High concentrations of gasoline are irritating to the lungs when breathed in and irritating to the lining of the stomach when swallowed. Gasoline is also a skin irritant. Breathing in high levels of gasoline for short periods of time or swallowing large amounts of gasoline may also cause harmful effects on the nervous system. These effects become more serious as the amount of gasoline breathed in or swallowed increases. Less serious nervous system effects include dizziness and headaches, while more serious effects include coma and the inability to breathe. Effects on the nervous system have also occurred in people exposed to gasoline vapors for long periods of time, either in their jobs or because they intentionally sniff gasoline for its ability to cause hallucinations. Harmful effects on the lungs can occur when a person swallows large amounts of gasoline because the gasoline in the stomach can enter the lungs during vomiting.

2.1.5.1 Health Hazard Data (8)

1. The major effect of exposure to gasoline is central nervous system depression and polyneuropathy.

2. Studies have shown that repeated exposure of laboratory animals to high concentrations of whole gasoline vapours at 67,262 and 2056 ppm has caused kidney damage and cancer of the kidney in rats and liver cancer in mice.

3. IARC has listed gasoline as possible carcinogenic (2B) to humans with limited evidence in humans in the absence of sufficient evidence in experimental animals. NIOSH lists gasoline as a carcinogen with no further classification.

4. N-heptane and cyclohexane cause narcosis and irritation of eyes and mucous membranes. Cyclohexane has been reported to cause liver and kidney changes in rabbits. N-heptane has been reported to cause polyneuritis following prolonged exposure.

5. ACGIH lists benzene as human carcinogen with assigned TLV of 0.5 ppm for 8 hour TWA and a STEL of 2.5 ppm; IARC, OSHA show sufficient evidence for classifying benzene as a human carcinogen, 29 CGR 1910.1028 for current PEL of 1 ppm and specific actions to take. Studies have shown that benzene can induce leukemia at concentrations as low as 1 ppm. Significant elevations of

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chromosomal aberrations have been collaborated among workers exposed to levels at mean concentrations less than 10 ppm. Based on risk assessment studies by Rinsky, an individual inhaling 1 ppm of benzene for 40 years, the odds of benzene-induced leukemic death were 1.7 times higher than those of unexposed workers.

6. MTBE is a mild irritant to the eye with an LC50 of 85 mg/m3 for 4-hr. exposure and an LD50 of ~4 ml/Kg (RATS). An increase in anaesthesia with increasing concentration (250,500 & 1000 ppm) was observed during a 90-day test exposure. ACGIH has listed MTBE as an animal carcinogen (A3) based on tests in experimental animals at relatively high dose levels, by routes of administration, at sites, of histological types, or by mechanisms not considered relevant to worker exposure. Available evidence suggests that MTBE is not likely to cause cancer in humans except under uncommon or unlikely routes and levels of exposure.

7. Trimethylbenzene (pseudocumene (1,2,4,) & mesitylene (1,2,5,)) has a PEL or TLV of 25 ppm 8-hr. TWA; the isomers may cause nervousness, tension, and anxiety and asthmatic bronchitis.

8. n-Hexane has been shown to cause polyneuropathy (peripheral nerve damage) after repeated and prolonged exposure, other hexanes show narcotic effects at 1000 ppm and are not metabolized like n-hexane.

9. Toluene can cause impairment of coordination and momentary loss of memory (200-500 ppm); Palpations, extreme weakness and pronounced loss of coordination (500-1500). The 100 ppm 8-hr. TWA and the 150 ppm STEL provides adequate protection.

10. The toxicological effects of ETBE and TAME have not been thoroughly investigated. ETBE and TAME are expected to be an inhalation hazard and a severe eye and moderate skin irritant

Some laboratory animals that breathed high concentrations of unleaded gasoline vapors continuously for 2 years developed liver and kidney tumors. However, there is no evidence that exposure to gasoline causes cancer in humans. There is not enough information available to determine if gasoline causes birth defects or affects reproduction.(6)

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2.1.5.2 Routes of Exposure (8)

Inhalation: Irritation of the upper respiratory tract with central nervous system stimulation possibly followed by depression, dizziness, headache, in coordination, anaesthesia, coma, and respiratory arrest. The threshold for immediate mild toxic effects is reported to be 900-1000 ppm.

Skin Contact: Defatting of the skin may occur with continued and prolonged contact. Irritation and burning sensation may occur on exposure to the liquid or high vapour phase exposure.

Skin Absorption: Benzene is absorbed directly through intact skin.

Eye Contact: Contact with liquid will cause severe burning sensation with temporary irritation and swelling of lids. Vapour at concentrations of 160-270 ppm in air will irritate the eyes.

Ingestion: Irritation of the mucous membranes of throat, esophagus and stomach which may result in nausea and vomiting; depression may occur, if absorbed (see inhalation symptoms above). If aspirated, chemical pneumonitis may occur with potentially fatal results.

2.2 BENZENE

2.2.1 General Information of Benzene (9)

Benzene is an aromatic hydrocarbon, which is the smallest and most stable aromatic compound. Molecular formula of Benzene is C6H6 and molecular weight equips 78.11. Common synonyms are annulene, benzine, benzole, benzol coal naphtha, cyclohexatriene, mineral naptha, motor benzol, phenyl hydride, pyrobenzol and pyrobenzole. It is a colorless liquid, highly flammable, non-polar liquid with an odor that is characteristic of hydrocarbons. It is thus a hydrophobic solvent that readily evaporates at room temperature and rapidly partition into liquid. The chemical structure, physical and chemical properties of benzene are shown in table 4.

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Table 4. The physical and chemical properties of benzene (9)

Properties	Value
Chemical structure	
CAS Number	71-43-2
Chemical formula	C6H6
Molecular weight	78.11
Physical form	Volatile, colorless, flammable liquid, aromatic carbon
Flash point	-11.1
Flammable limits	1.3-7.1
Boiling point	80.1 °C at 760 mmHg
Melting/Freezing point	5.5 °C
Density	0.878 g/l at 15 °C
Vapor pressure	13.3 kPa (0.125 atm)
Solubility:	
Water	1.8 g/l
Non-aqueous solvents	Miscible with most solvent
Log octanol/water partition co-efficient	1.56-2.15
Odor threshold:	
In air	4.8-15.0 mg/m3
In water	2.0 mg/l
Taste threshold (in water)	0.5-4.5 mg/l
Air concentration conversion factor	3.2 mg/m3=1 ppm at 20 °C

2.2.2 Uses (9),(10)

In the past, benzene was used widely as a solvent, but this use is declining in most developed countries; it represents < 2% of current use (9). However, benzene is still used as a solvent in scientific laboratories, printing and lithography, paint, rubber

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dry cleaning, adhesives and coatings, detergents, extraction and rectification, preparation. It is also used in the graphic arts industries, as thinner for paints, as degreasing agent and used in the production of drugs, dyes, insecticides, and plastics. In tire industry and shoe factories, benzene is used extensively. Benzene is also used as an additive for motor fuels to increase the octane and is used as a raw material in the synthesis of styrene (polystyrene plastic and synthesis rubber), phenol (phenolic resins), cyclohexane (nylon), aniline, maleic anhydride (polyester resins), alkylbenzenes (detergents), chorobenzenes, and other products (10). However, for many solvent used, benzene has been replaced by less toxic organic solvents.

2.2.3 Environmental Fate (10),(11),(12)

The predominant sources of total benzene emissions in the atmosphere are gasoline fugitive emissions and gasoline motor vehicle exhaust. Mobile sources contribute 85 percent and industry-related stationary sources 15 percent of the emissions (11). In the United States, automobile sources accounted for 85% of the total benzene emissions. Of this amount, 70% comes from exhaust, 14% from evaporative emission, and 1% from motor vehicle refueling (12). Due to its volatile nature, benzene is released to soil; it will be mobile in the soil and may leak to ground water. If benzene is released to soil, it will be subjected to rapid volatilization; the half-life for evaporation depends on the wind speed and temperature. Once benzene is released to the atmosphere, it will exist predominantly in the vapor phase. Gas-phase benzene will be photo degraded with a half-life of 13.4 days. Benzene is fairly soluble in water and is removed from the atmosphere by rain (10).

2.2.4 General Population and Occupational Exposure (9),(13)

Most of general populations are exposed to benzene through a variety of sources. The most important sources of exposure are primarily through inhalation of contaminated air particularly in areas of heavy automobile traffic and vicinity of gasoline stations including storage and distribution of petrol, home use of solvents including household cleaning agents and glues and included tobacco smoke from both active and passive smoking (9). Bases on extensive studies in the USA, it appears that facilities manufacturing chemicals, drinking water, food and beverages and petroleum

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refining operations play minimal roles in the total exposure of general population to benzene (13).

Occupational exposure to benzene has decreased greatly over the past 40 years as a result of lowering occupational exposure as a solvent. Currently, significant exposure to benzene is limited to workers in the petroleum, coal (coking operations), and synthetic chemical industries. Under the current OSHA PEL, workplace exposure may not exceed 1.0 ppm. NIOSH has recommended a workplace standard of 0.1 ppm (14). In addition, the ACGIH-TLV is 0.5 ppm as an 8-hr TWA and 2.5 ppm as a STEL (15).

2.2.5 Health Effect (16)

When you breathe contaminated air with benzene, it can enter your body through your lungs and enters your bloodstream. It can enter your stomach or intestines when you eat food or drink water that contains benzene. Benzene can enter your body through skin contact with benzene-containing products such as gasoline. Animal studies show that benzene taken in by eating or drinking contaminated foods, including passing benzene through your skin behaves similarly in the body. Once in the bloodstream, benzene travels throughout your body and can be temporarily stored in the bone marrow and fat. Benzene is converted to products, called metabolites, in the liver and bone marrow. Some of the health effects of benzene exposure are believed to be caused by these metabolites. Most of the metabolites of benzene leave the body in the urine within 48 hours after exposure.

2.2.5.1 Acute Toxicity in Humans (16),(17),(18)

Humans have confirmed a relatively high tolerance for acute exposure to benzene. Short exposure (5–10 minutes) to very high levels of benzene in air (10,000–20,000 ppm) can result in death. Lower levels (700–3,000 ppm) can cause drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness (16). The primary acute response to benzene exposure involves adverse effects on the central nervous system (CNS), including dizziness, giddiness, exhilaration, nausea, vomiting, headache, drowsiness, staggering, loss of balance, narcosis, coma, and death (17). Table 5 presents a summary of published case reports of toxicity associated with various airborne concentrations of benzene (18).

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Table 5. Adverse effects in humans after short-term exposure to various concentrations of benzene vapor (18).

Benzene concentration, (ppm)	Duration of exposure, (hr)	Effects observed
25	8	None
50-150	5	Headache, lassitude, weariness
500	1	Symptoms of illness
1,500	1	Serious symptoms
1,500-3,000	Several hours	Slight symptoms
1,550-3,100	6	No serious effects
1,570-3,130	Several hours	Slight symptoms
3,000	0.5	Endurable
3,000	0.5-1	Dangerous
3,000-4,700	1	Maximum concentrations that can be inhaled for 1 hr with out serious disturbance
3,130-4,700	0.5-1	Maximum concentrations for exposures for this period of time
4,650	0.5	Listlessness and confusion
4,700	0.5	Confusion
6,190-9,300	Few hours	Definite symptoms of poisoning
6,200-9,300	0.5-1	Immediate or subsequent death
7,500	0.5-1	Dangerous to life
6,200-9,300	Few hours	Loss of consciousness
19,000-20,000	Short exposure	Rapidly fatal

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2.2.5.2 Chronic Toxicity in Humans (16)

Since the nineteenth century, chronic benzene exposure has been known to cause hematological effects. Long periods of exposure benzene may experience harmful effects in the tissues that form blood cells, especially the bone marrow. These effects can disrupt normal blood production and cause a decrease in important blood components. A decrease in red blood cells can lead to anemia. Long-term exposure to relatively high levels of benzene in the air can cause cancer of the blood-forming organs; called leukemia. The Department of Health and Human Services (DHHS) has determined that benzene is a known carcinogen. The International Agency for Cancer Research (IARC) has determined that benzene is carcinogenic to humans, and the EPA has determined that benzene is a human carcinogen.

Exposure to benzene may be harmful to the reproductive organs. Some women workers who breathed high levels of benzene for many months had irregular menstrual periods. When examined, these women showed a decrease in the size of their ovaries. However, exact exposure levels were unknown, and the studies of these women did not prove that benzene caused these effects. It is not known what effects exposure to benzene might have on the developing fetus in pregnant women or on fertility in men. Studies with pregnant animals show that breathing benzene has harmful effects on the developing fetus. These effects include low birth weight, delayed bone formation, and bone marrow damage

2.3 Exposure Model (19)

2.3.1 Aspects Of Exposure Modeling

Exposure models can be developed to estimate exposures and doses of individuals, defined population groups, or entire populations. Exposure may be estimated as a continuous variable or integrated over time ranging from minutes to a lifetime. The modeled outputs may include mean or median values, distribution parameters (standard deviations, quartiles, ranges), or entire distributions. Consequently, exposure models vary widely in complexity, approach, inputs, and outputs.

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2.3.1.1 Conceptual models

An exposure model must be based on a credible theoretical conceptual model (and scenario). A conceptual model is a description of predicted relationships between exposure targets such as humans and the environmental agents to which the targets may be exposed. It is usually based on known or anticipated causal relationships between the input and the output events (the exposure scenario). The conceptual model is implemented through the development of equations and algorithms that quantify these relationships. The implementation should reflect the conceptual model. However, environmental exposures are often affected by many factors that are difficult to describe quantitatively, and compromises and simplifications are often necessary. Results from the implemented model may not be reliable even when the conceptual model behind the implementation is valid.

2.3.1.2 Computational elements of a model

Implemented exposure models are quantitative constructs that estimate the relationships between measurable events. The measurable events are entered into the model as input variables. These inputs must be causally related to other events, which are the outputs or result variables of the model. The relationships between the inputs and outputs are described in the model using algorithms, equations, and intermediate variables. These five components of a model — the input variables, the algorithms, the equations, the intermediate variables, and the output variables — are depicted in Figure 1.

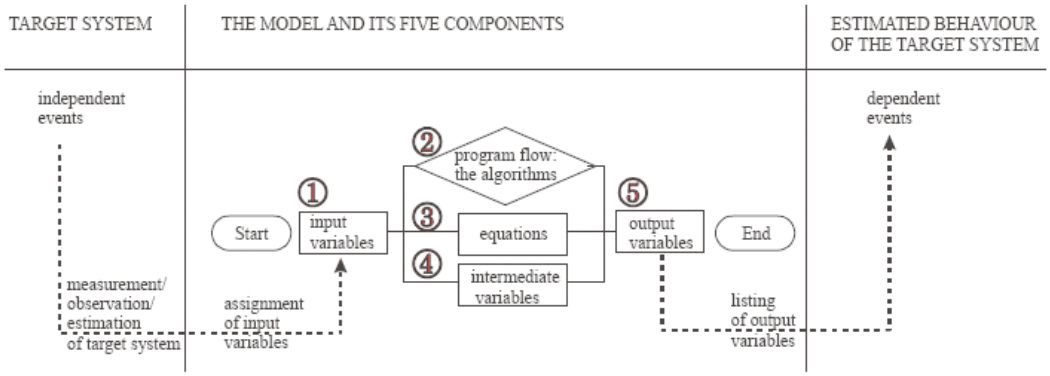

Figure 1. Five components of a model.

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If the events in the target system do not vary in logical relation or correlate with each other, there is nothing to be modeled. Figure 2 shows different relationships between correlating variables. In case 1, there is a correlation between the two events, but the cause of the correlation is not known. In case 2, there is a cause–effect relationship. In case 3, both effects are caused by the same known cause and thus may be correlated. Models based on causal relationships (case 2) are generally more reliable than models based only on statistical associations (case 1). Statistical correlation can result from a cause affecting both of the correlating events, which, however, do not depend on each other (case 3).

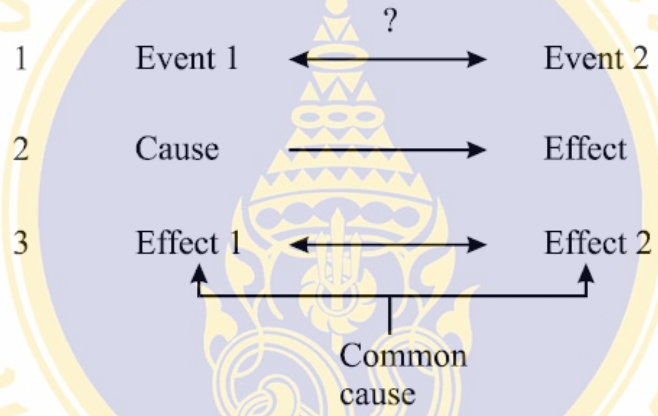

Figure 2. Different relationships between two variables (events).

Models are best suited to study how the changes in the input variables are reflected in the outputs — i.e., for sensitivity analyses. A model can be linked with other models or combined with general knowledge about how prior events are reflected in the model inputs and how the model outputs affect subsequent events. For example, an air concentration input to a model that estimates the amount of pollutant inhaled may itself be modeled using a dispersion model. An intake dose output may be used as input to a toxic kinetic model that estimates the dose to a target organ. This is shown in Figure 3. However, no model can be used to assess the effect of variables unrelated to either model inputs or model outputs. Thus, listing of the model input and output variables define the main application domain of a model.

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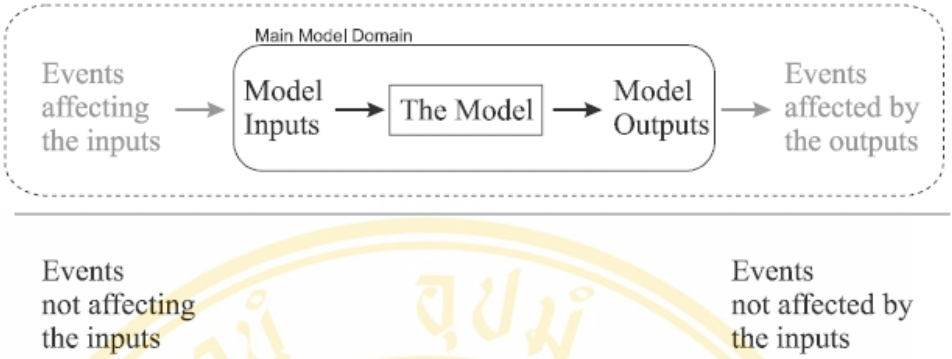

Figure 3. Relationships between input and output variables.

2.3.2 Approaches to exposure modeling

There are many different ways to classify models. A consensus appears to be developing around the following classification scheme.

2.3.2.1 Mechanistic versus empirical models

The mechanistic model simulates the behavior of a pollutant in the environment and in target organisms as it is transported and undergoes physical and chemical transformations. The empirical model predicts concentrations and exposures based on statistical relationships between concentrations in relevant media that are observed in measurement studies.

A mechanistic model uses process, physicochemical characteristics, and mass balances to predict exposures. Such a model is a mathematical construct, which attempts to mimic the physical and chemical reality relevant for the exposure of interest. A mechanistic model can produce single point estimates of outputs by using single point values for input variables, or it can produce distributions of output variables by sampling from distributions of input variables (i.e., the probabilistic approach). Mechanistic models are built on causal relationships represented by equations. Results can be calculated even when there are no measurements of the output variables. Thus, they can be applied in situations where no measured exposure data are available or where such measurements are even impossible, as in an assessment of past and future exposure scenarios.

An empirical model is a mathematical representation of the relationship between input and output variables based on historical measurements. An example of

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such a model is a regression between ambient air quality and personal exposure. In the simplest form, the empirical model contains a constant term β0 and a coefficient term β1. More complex multiple regression models can include the concentrations in many microenvironments and dummy variables for yes/no-type parameters, such as smoking, work on a dairy farm, connection to a municipal water supply, ethnic diet, etc. The terms of the empirical model are specific to the data set from which they have been calculated, and there are no grounds other than expert opinion with which to assess if they can be used to calculate exposures in some other system (location/ population), or even in the same system at another time.

Empirical models do not require or imply any causal relationships between the model variables. While a mechanistic model would need lengthy algorithms and calculations to assess how time spent in traffic affects exposures to a traffic-originating pollutant, such a relationship, given the required data set, can be easily described by an empirical model using statistical inferences. While an empirical model usually contains no construct reflecting the physical/chemical phenomena that cause the exposures, it does incorporate the interdependencies that exist in the measured data, regardless of whether they are known or considered by the modeler.

Weakness of empirical models is that they require both input and output variables to be known in a model development system before the model can be built. The best area of application of empirical models is in descriptive data analysis. Statistical methods can be used to explore and identify correlating phenomena. Further studies and conceptual methods can then be used to reveal the true causal mechanisms behind the correlations. Then, when the causal mechanisms are known, process equations can be written and mechanistic models developed to describe these relationships.

2.3.2.2 Deterministic versus stochastic (probabilistic) models

Mechanistic and empirical models can be classified as deterministic or stochastic (probabilistic). A deterministic model is one in which the variables are given fixed values so that the system is at any time entirely defined by the initial conditions chosen. It does not allow for random fluctuation in the input variables. A given set of input variables produces a fixed output.

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A stochastic (probabilistic) model is one that takes into consideration the presence of some randomness in one or more of its input parameters or variables (Swinton, 1999). It predicts the probabilities of occurrences of exposures and/or effects in a population. Random model input variables are represented as statistical distributions from which values are selected randomly and substituted into the equations of the model to produce an output. This process is repeated, usually several thousand times, to produce results in the form of a probability density function. Where possible, correlations in input variables must be considered. A deterministic model represents a single repetition of a stochastic model.

Typically, stochastic models are built on a mechanistic framework, although in principle empirical models can also be stochastic. In contrast to deterministic models, which assess exposure to a single individual, such as the maximally exposed individual, stochastic models usually deal with the variability in exposure and dose in a population. Individuals and events are combined into similar groups, and statistical parameters and distributions are used to describe the input variables for each group. The output is a distribution of exposures or doses for each group. Statistics of the distribution, such as the median, mean, and 95th percentile exposure, may be reported.

Rather simple stochastic models can be powerful and accurate population exposure assessment tools if the input variables (e.g., time spent in microenvironments/activities, intake rates, and exposure concentrations) are independent of each other, and if the sequences of the exposure events are irrelevant to the exposure. If these conditions are violated, the models either become more complex or may produce erroneous output (exposure or dose) distributions. More advanced probabilistic modeling techniques can also deal with intercorrelated input variables.

2.3.2.3 Hybrid models

Based on the definitions given above, any model, no matter how complex, is either deterministic or stochastic. If one or more input variables in the model fluctuate randomly, the output will be a probability density function, and the model is stochastic by definition. However, complex models often combine aspects of empirical and mechanistic models. A complex concentration model will generally be

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mechanistic, but the model may use empirical submodels to assign values to some of the input variables. Thus, many models are hybrids composed of empirical and mechanistic submodels.

2.3.3 Criteria for selecting a model

Ryan (1991) lists the following criteria affecting the selection of a model and states that they are often in direct conflict with each other:

- mathematical simplicity
- computational simplicity
- interpretability
- consistency (the ability to use a single model for many cases)
- accuracy in prediction

2.3.4 Exposure model applications

Exposure models can use whatever techniques and data are available to predict the properties of the immediate environment of humans for some specified purpose or need. Only after specifying the purpose and requirements and assessing the availability of data can one define the specifications for the exposure model for an application.

There are three important applications of exposure models:

1. Epidemiological studies: Epidemiology is the study of patterns and distributions of disease in human populations with the aim of determining causes of disease. To investigate links between disease and exposure to environmental agents, a measure or estimate of exposure is needed for each individual in the study. Exposure metrics can be very simple. A simple categorization of subjects by whether or not one is exposed to microbes in drinking-water or lives in the neighborhood of a steel mill may be sufficient to test a hypothesis relating to exposure and disease. However, there is often a need for more refined quantification of exposure (e.g., to develop dose–response assessments). When exposure information is based on subjects' recall and historical monitoring data, exposure models are needed to estimate individual and group exposures.

2. Risk assessments to support risk management decisions:

Exposure assessment is an integral part of risk assessments done in support of risk management decisions. A comprehensive conceptual model or scheme for risk

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assessment and risk management as published by the US National Academy of Sciences (NAS) in 1983 (NRC, 1983). The NAS Paradigm succeeded in setting a widely agreed framework for risk assessment / risk management, and it has had broad applications to environmental agents ranging from carcinogenic compounds to non-carcinogens, mixtures, radiation, microbes, and other environmental agents. The European Commission (EC) Directive 93/67/EEC "lays down the principles for assessment of risks to man and the environment of chemicals (or substances notified in accordance with Council Directive 67/548/EEC)." According to the NAS Paradigm and the EC Directive 93/67/EEC, formal risk assessment is divided into four activities: hazard identification, dose (concentration) – response (effect) assessment, exposure assessment, and risk characterization. In some assessments, the most exposed individual is targeted, in other cases, a sensitive subgroup or the whole population. Distributions of exposure across the population are often needed. Therefore, exposure models are used widely in risk assessments to support risk management decisions. For example, when alternative future risk management approaches are being compared, exposure modeling is the only way to quantitatively estimate future exposures to support these important comparisons. The exposure models used for these comparisons must include as inputs those parameters that the policies intend to change (e.g., automobile exhausts) as well as those parameters that are expected to change as a consequence of the regulation (e.g., transportation patterns).

3. Assessment of the efficacy of environmental risk management policies:

The efficacy of risk management policies is receiving increased attention. Governments are attempting to evaluate the public health achievements of the implemented policies against risk reduction goals. Measurement of the achieved mortality and morbidity reduction due to implementation of risk reduction policy is, however, usually impossible (with notable exceptions — e.g., Clancy et al., 2002). Implementation of regulations takes years, and other simultaneous changes in diseases, treatments, demography, and other environmental parameters will inevitably, and in many unknown ways, also change population mortality and morbidity. Regulatory targets are usually set based on reduced emissions, concentrations (e.g., in air or water), or reduction of exposure rather than reduction of disease, because these can be planned, modeled, managed, measured, and verified independently from other

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developments in the society. Exposure models can play an important part in assessing these changes.

2.4 Literature Cite (20-26)

Navasumrit, P.and et al. (20) studied exposure to benzene in air is a concern in Thailand, particularly since it was observed that the incidence of blood-related cancers, such as leukemia and lymphoma, has increased in the past few decades. In Bangkok, the mean atmospheric levels of benzene on main roads and in schools were 33.71 and 8.25 ppb, respectively, while in gasoline service stations and petrochemical factories the mean ambient levels were 64.78 and 66.24 ppb, respectively. Cloth vendors (22.61 ppb) and grilled-meat vendors (28.19 ppb) working on the roadsides were exposed to significantly higher levels of benzene than the control group (12.95 ppb; $p < 0.05$). Bangkok school children (5.50 ppb) were exposed to significantly higher levels of benzene than provincial school children (2.54 ppb; $p < 0.01$). Factory workers (73.55 ppb) and gasoline service attendants (121.67 ppb) were exposed to significantly higher levels of benzene than control workers (4.77 ppb; $p < 0.001$)

Periago, J.F., and Prado, C.(21) researched in two phases. The first phase was carried out in 2000, after application of the new legal regulation limiting the benzene concentration in gasoline. In this case, an occupationally exposed population of 28 service station attendants was sampled in July, with a mean ambient temperature of 30-31°C. In the second phase, 19 exposed subjects were sampled in July 2003, one of the warmest months in recent years with mean temperatures of 35-36°C during the time of exposure monitoring. The results were then compared with those obtained in 1995, for similar summer weather conditions (environmental temperature between 28 and 30°C). A significant relationship between the volume of gasoline sold and the ambient concentration of aromatic hydrocarbons was found for each worker sampled in all three of the years. Furthermore, a significant decrease in the environmental levels of BTXs was observed after January 2000, especially in the case of benzene, with mean time-weighted average concentrations for 8 h of 736 $\mu g/m^3$ (range 272-1603) in 1995, 241 $\mu g/m^3$ (range 115-453) in 2000 and 163 $\mu g/m^3$ (range 36-564) in 2003, despite the high temperatures reached in the last mentioned year.

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Egeghy, P.P. and et al.(22) measured benzene exposure and uptake (via benzene in exhaled breath) among 39 self-service customers using self-administered monitoring, a technique rarely used to obtain measurements from the general public (130 sets of measurements were obtained). Benzene exposures averaged 2.9 mg/m^3 (SD = 5.8 mg/m^3; median duration = 3 min) with a range of < 0.076-36 mg/m^3, and post exposure breath levels averaged 160 $\mu g/m^3$ (SD = 260 $\mu g/m^3$) with a range of < 3.2-1,400 $\mu g/m^3$. Log-transformed exposures and breath levels were significantly correlated ($r = 0.77$, $p < 0.0001$). This research used mixed-effects statistical models to gauge the relative influences of environmental and subject-specific factors on benzene exposure and breathe levels and to investigate the importance of various covariates obtained by questionnaire. Model fitting yielded three significant predictors of benzene exposure, namely, fuel octane grade ($p = 0.0011$), duration of exposure ($p = 0.0054$), and season of the year ($p = 0.032$). Likewise, another model yielded three significant predictors of benzene concentration in breath, specifically, benzene exposure ($p = 0.0001$), pre-exposure breath concentration ($p = 0.0008$), and duration of exposure ($p = 0.038$). Variability in benzene concentrations was remarkable, with 95% of the estimated values falling within a 274-fold range, and was comprised entirely of the within-person component of variance (representing exposures of the same subject at different times of refueling). The corresponding range for benzene concentrations in breath was 41-fold and was comprised primarily of the within-person variance component (74% of the total variance). Our results indicate that environmental rather than interindividual differences are primarily responsible for benzene exposure and uptake during automobile refueling.

Hakkola, M.A., and Saarinen, L.H. (23) studied the difference in the exposure of customers to gasoline and oxygenate vapors during refueling in service stations with and without vapor recovery systems. Field measurements were carried out at two self-service stations. One was equipped with Stage I and the other with Stage II vapor recovery systems. At Stage I stations there is vapor recovery only during delivery from road tanker, and at Stage II stations additional vapor recovery during refueling. The exposure of 20 customers was measured at both stations by collecting air samples from their breathing zone into charcoal tubes during refueling with 95-octane reformulated gasoline. Each sample represented two consecutive refuelings. The

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samples were analyzed in the laboratory by gas chromatography using mass-selective detection for vapor components. The Raid vapor pressure of gasoline was 70 kPa and an oxygen content 2 wt%. Oxygenated gasoline contained 7 percent methyl tert-butyl ether (MTBE) and 5 percent methyl tert-amyl ether (MTAE). The geometric mean concentrations of hydrocarbons (C3-C11) in the customers' breathing zone was 85 mg/m3 (range 2.5-531 mg/m3) at the Stage I service station and 18 mg/m3 (range < 0.2-129 mg/m3) at the Stage II service station. The geometric mean of the exposure of customers to MTBE during refueling at the Stage I service station was 15.3 mg/m3 (range 1.8-74 mg/m3), and at the Stage II service station 3.4 mg/m3 (range 0.2-16 mg/m3). The differences in exposure were statistically significant ($p < 0.05$). The exposure level of customers at the Stage II station during refueling was circa 20-25 percent of the exposure at the Stage I service station when conditions were equal and no other confounding factors such as leaks or spills were presented.

Chen, M.-L., and et al.(24) evaluated the relationship between the breath concentrations of, and personal exposure to, toluene, xylene and ethylbenzene of thirty workers from ten gasoline stations. Personal exposure air samples and workplace samples were collected simultaneously. Each subject provided a sample of exhaled breath after his or her personal exposure air was sampled. Twenty-five personal air, 17 workplaces and 30 breath samples were collected in this study. Results indicated that breath concentrations of toluene and xylene were significantly correlated with personal monitoring concentrations. Furthermore, multiple regression analysis showed that exhaled toluene levels were highly influenced by personal toluene concentrations and the amount of personal gasoline sold ($r^2 = 0.762$), while exhaled xylene levels depended on wind speed and personal xylene exposure concentrations ($r^2 = 0.665$). Exhaled ethylbenzene levels were too low to present a relationship between concentrations and personal exposure levels. The exhaled toluene, xylene and ethylbenzene concentrations ranged from 4.3 to 41.8, 0.9 to 13.9, and 0.2 to 6.5 ppb, and the corresponding personal monitoring concentrations ranged from 60.3 to 572.3, 16.4 to 156.6, and 10.7 to 136.6, respectively. The average number of symptoms per person, according to neurotoxic questionnaire 16 (abbreviated as Q16) was 4.1 and six workers showed over six symptoms in Q16. This study suggests that exhaled toluene and xylene levels are suitable for use as biological exposure indices even at the ppb-

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level of exposure. Gasoline service workers are exposed to high levels of volatile organic compounds (VOCs) and the potential threats to their neurological systems deserve further investigation.

Vainiotalo S and Ruonakangas A.(25) studied of tank truck drivers' exposure to gasoline vapors by collecting breathing zone samples during loading and unloading of gasoline. The field studies were conducted at three dispatches and at seven service stations in Finland. The gasoline included in the study (95, 98, 99 research octane number, RON) was of reformulated or oxygenated grade containing about 2% (w/w) oxygen and 0.5-1.5% (v/v) benzene. The sampling times ranged from 16 to 57 min (mean 35 min), and time-weighted average concentrations for a 30-min period were calculated. The GM concentrations of hexane, benzene, and toluene were in the range of 0.25-2.3 mg/m3, 0.15-0.28 mg/m3, and 0.73-1.7 mg/m3, respectively. Multiple regression analysis yielded an r2 value of 0.98 for the daily mean concentration of toluene and correspondingly 0.94 for benzene when daily wind speed (0.1-3.7 m/sec) and daily air temperature (-7.4(-)+17.2 degrees C) were used as independent variables. The average number of gasoline loads per tank truck was 2.5, corresponding to 23,000 L of gasoline.

Foo, Swee-Cheng (26) studied the exposure of gasoline station attendants to short-term exposure levels (STEL) of 0.064-179 ppm. Their 8-h time-weighted averaged (TWA) exposure ranged from 0.028 to 0.71 ppm. For motorcar service mechanics, TWA exposure levels ranged from 0.014 to 1.7 ppm. The exposure of drivers of gasoline delivery tankers ranged from 0.08 to 2.37 ppm for personal TWA exposure over the whole workshift. For local people not occupationally exposed to gasoline or other benzene-containing volatile chemicals exposure from the ambient environment ranged from 0.0023 to 0.027 ppm. Gasoline usage also contributed to the contamination of surface water with benzene. Benzene levels in water samples taken from drains leading from gasoline stations were between 1.1 and 40.4 $\mu g\ l^{-1}$.

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CHAPTER III
METERIALS AND METHODS

This study is aimed to develop the estimated benzene and toluene exposure model of gasoline service station attendants. The method is divided into 2 parts : data collection at gasoline service station and analysis at laboratory. The general information of subjects was collected from questionnaires. Benzene and toluene concentrations in air were collected by personal air sampling pump and analyzed by a gas chromatograph (GC). Gasoline was collected from service station on the sampling day and analyzed quantity of benzene and toluene by gas chromatograph (GC) .

3.1 Population and sample

The samples of this study are the workers in gasoline service station who has duties as a gasoline filler.

3.2 Sample size

Number of sample size were calculated from the formula below:

$$n_o = Z^2_\alpha \times s^2 / d^2$$

Where

n_o = Number of sample size

Z = The value from Z table

s^2 = The variance of benzene concentration in working condition form the previous study

d = The difference of the population and sample means of benzene concentration

In this study the confidence internal will be defined at 95%, the variance of benzene = $(2.47)^2$, d = 0.5 and Z = 1.96.

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$n_o = (1.96)^2 * (2.47)^2 / (0.4)^2$

$n_o = 146.48$

Thus, the sample size of this study is at least 147.

3.3 Apparatuses and chemical reagents

3.3.1 Apparatuses

3.3.1.1 Gas chromatograph (GC-2010, Shimadzu, Kyoto, Japan) equipped with flame ionization detector, and integrator, a DB-1 capillary column (30 m x 0.25mm I.D., J&W, USA)

3.3.1.2 Air compressor (SWAN, Model DR-115, Taiwan)

3.3.1.3 Fume hood

3.3.1.4 Soap bubble meter

3.3.1.5 Laboratory glass ware, i.e. pipettes, beakers, volumetric flasks. and vials

3.3.1.6 SKC personal air sampling pump (Model 222-3, SKC Inc., USA)

3.3.1.7 Gilian personal air sampling pump (Model LFS 113D, Gilian Instrument Corp., USA)

3.3.1.8 Activated charcoal tubes (SKC -226-09, SKC Inc., USA)

3.3.1.9 Glass bottle, 100 ml

3.3.1.10 Wind speed measurement

3.3.1.11 Relative Humidity measurement

3.3.1.12 Barometer

3.3.1.13 Parafilm

3.3.1.14 Microsyringe 10 µl (Hamilton 80300).

3.3.2 Chemical reagents

3.3.2.1 Benzene (AR grade, Merck, Germany)

3.3.2.2 Toluene (AR grade,

3.3.2.3 Carbon disulfide (AR grade, Merck, Germany)

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3.3.2.4 Purified helium (Height purity grade, Praxair, Thailand)

3.3.2.5 Purified hydrogen (Height purity grade, Praxair, Thailand)

3.3.2.6 Purified nitrogen (Height purity grade, Praxair, Thailand)

3.3.2.7 Air filtered

3.3.2.8 Distilled water

3.4 Data collection

Benzene in gasoline vapor was sampling according to NIOSH Method 1501 (27). The working condition during sampling, namely wind speed, air temperature, vapor pressure and relative humidity were measured. In addition, amount of gasoline sold on the sampling day was also collected from each sampling service station.

3.4.1 Sample collection at gasoline service station

3.4.1.1 The personal air sampling pump with an activated charcoal tube in line was calibrated. Before sampling, the ends of the charcoal tube were broken, then one end was attached to a personal air sampling pump with flexible tubing, which suck up air through charcoal tube at a flow rate of 0.15 L/min. This device was set up at breathing zone of gasoline service attendants as personal air sampling for 8 to 12 hours in workday following NIOSH method number 1501. After sampling, the charcoal tubes were capped and packed securely in a plastic bag for shipment. Field blank charcoal tubes were used without drawing the air into the tubes (27). The charcoal tubes and field blank charcoal tubes were stored in the laboratory at -35 °C until analysis.

3.4.1.2. Gasoline octane 91 and 95 in gasoline service station were sampling from filling nozzle into a glass bottle on the sampling day. Then it was closed with the steel cover and sealed with paraffin before shipment. The bottles of gasoline were stored in the laboratory at -35 °C until analysis.

3.4.1.3 The working conditions at service station were measured. We measured a wind speed with wind speed instrument at breathing zone level of subject, Temperature and relative humidity at service station ware measured at working area

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every 40 min. Vapor pressure was also measured every 1 hour with a barometer at the working area

3.4.1.4 Amount of gasoline 91 and 95 sold on the sampling day was collected. After the end of shift, we inquired the manager of service station about the amount of gasoline sold on that day.

3.4.2 Determination of benzene and toluene by gas chromatograph

3.4.2.1 Operating condition of GC for analysis of benzene and toluene concentrations in air sample.

The operating conditions for gas chromatograph were set up for analysis of benzene and toluene concentrations in air:

Column :	DB^{TM} – 1 capillary column (30m * 0.25-mm ID)	
Detector :	Flame ionization detector	
Temperature :	Column	40 °C hold time 7.5 min
		200 °C hold time 5.0 min
	Oven ramp rate	40 °C/min
	Injection port	120 °C
	Detector	250 °C
Carrier gas :	Helium	1.20 ml/min
Purge gas :	Nitrogen	3.0 ml/min
Spilt ratio :		30.0

3.4.2.2 The standard stock solution for analysis of benzene and toluene concentrations in air sample.

For a standard stock solution, 4.0 µl benzene and 5.0 µl toluene was added into the 10 ml volumetric flask containing small amount of carbon disulfide then carbon disulfide was added to the mask of 10 ml. The benzene and toluene concentration in this stock solution were 0.3509 and 0.4313 mg/ml respectively.

3.4.2.3 Calibration curve for benzene and toluene concentration in air sample

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The calibration curve was consisted of five concentrations of benzene and toluene. A series of benzene and toluene standard was prepared by diluting the stock standard solution (0.1 ml, 0.2 ml, 0.4 ml, 0.6 ml and 0.8 ml) with carbon disulfide to a total volume of 3 ml. One microliter of sample aliquot was injected manually into the GC using solvent flush technique. The peak area of benzene and toluene ware measured. The mass of benzene and toluene was calculated, and was plotted against the integrated peak area.

3.4.2.4 Analytical method for benzene and toluene concentrations in air sample

The front and back sorbent sections of the charcoal tubes were placed in separated vials. The glass wool and foam plug ware discarded. Three milliliter of carbon disulfide was added to each vial. The vial was capped immediately by a crimp cap and allowed to stand at least 30 minute with occasional agitation. One microliter of sample was injected manually into the GC using solvent flush technique. The peak area of benzene and toluene ware measured. The mass of benzene and toluene ware calculated. The calibration curves ware plotted between the concentrations of benzene and toluene and the integrated peak area of benzene and toluene.

3.4.2.5 Calculation for benzene and toluene concentration in air sample

The masses of benzene found in the sample front (Wf) and back (Wb) sorbent sections; mg of benzene (Corrected for Desorption Efficiency) was determined including the average media blank front (Bf) and back (Bb) sections. If the Wb mass > Wf/10 has to report as breakthrough and sample loss possibility.

Benzene concentration in air volume sampled, V(L) was calculated by the equation below. (27)

$$C = \frac{(Wf+Wb-Bf-Bb) \times \text{desorption volume (ml)} \times 10^3, \text{ mg/m}^3}{V}$$

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3.4.3 Operating condition of GC for analysis of benzene and toluene quantity in gasoline

3.4.3.1 The operating conditions for gas chromatograph set up for analysis benzene and toluene quantity in gasoline were as follows:

Column :	DB^{TM} – 1 capillary column (30m * 0.25-mm ID)	
Detector :	Flame ionization detector	
Temperature :	Column	40 °C hold time 9.0 min
		200 °C hold time 5.0 min
	Oven ramp rate	40 °C/min
	Injection port	120 °C
	Detector	275 °C
Carrier gas :	Helium	0.8 ml/min
Purge gas :	Nitrogen	3.0 ml/min
Spilt ratio :		100.0

3.4.3.2 The standard stock solution for analysis of benzene and toluene quantity in gasoline

For the standard stock solution, 0.02 ml benzene and 0.04 ml toluene was pipetted into the 10 ml volumetric flask containing small amount of carbon disulfide then diluted to 10 ml with carbon disulfide. The benzene and toluene concentrations in this stock solution were 17.55 and 34.50 mg/ml respectively.

3.4.3.3 Calibration curve for analysis of benzene and toluene quantity in gasoline

The calibration curve was consisted of five concentrations of benzene and toluene. A series of benzene standard was prepared by diluting the stock standard solution (0.05 ml, 0.1 ml, 0.2 ml, 0.4 ml and 0.8 ml) with carbon disulfide to a total volume of 1 ml. One microliter of sample was injected manually into the GC equipment using solvent flush technique. The peak area of benzene and toluene was

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measured. The mass of benzene and toluene ware calculated. The calibration curves of benzene and toluene ware plotted.

3.4.3.4 Analytical method for analysis of benzene and toluene quantity in gasoline

Gasoline 0.1 milliliter was put in vials and 0.9 ml carbon disulfide was added and the solution was shake. One microliter of solution was injected manually into GC system using solvent flush technique. The peak area of benzene and toluene ware measured. The mass of benzene and toluene ware calculated from the calibration curve plotted between the concentrations of benzene and toluene corresponding to their integrated peak area.

3.5 Statistical analysis

3.5.1 Descriptive statistic for summary all data.

3.5.2 Comparison of atmospheric benzene and toluene exposures at different working condition of gasoline service stations using t-test or Mann-whitney test according to the result of data

3.5.3 The correlation was performed between benzene and toluene exposure and each factor using Pearson's product moment correlation coefficient or Spearman's rank correlation coefficient according the result of data.

3.5.4 A benzene exposure predicted model of service station attendant was carried out using multiple regression analysis at 95% confident interval.

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CHAPTER IV
RESULT

The main objective of this research was to study the level of benzene and toluene exposure and environmental factors, influencing benzene and toluene exposure of service station attendants.

The results of this study were divided into 8 parts as follows:

Part 4.1 Chromatogram of benzene and toluene concentration in air and gasoline

Part 4.2 Calibration curves for determination of benzene and toluene in air and gasoline

Part 4.3 Desorption efficiency of benzene and toluene from charcoal

Part 4.4 The characteristics of gasoline service stations and service station attendants

- General characteristic of subjects
- Factors of gasoline service stations, i.e. environmental conditions, amount of gasoline sold and benzene content in gasoline.

Part 4.5 Benzene and toluene concentrations in gasoline and in breathing zone air.

Part 4.6 Comparison of atmospheric benzene and toluene exposures at different factors of gasoline service stations.

Part 4.7 The benzene exposure estimated model of station attendants.

Part 4.8 The toluene exposure estimated model of station attendants

4.1 Chromatogram of benzene and toluene concentrations in air and gasoline

4.1.1 Chromatogram of benzene and toluene concentrations in air

Concerning the chromatogram of chemicals in air, benzene and toluene standard solution were prepared and analyzed by gas chromatography. The chromatographic profiles obtained from benzene and toluene concentrations in air which used as standard sample showing benzene and toluene peak separated at the retention time of 3.61 and 6.34 min, respectively (Fig. 4). Chromatograms of pure

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carbon disulfide (Analysis Grade) have an unknown peak which has a retention time at 3.614 min (Fig.5). Chromatograms of blank and air samples at breathing zone of one service attendant subject participated in the study; benzene and toluene peak separated nearly completely as shown in Fig.6, and 7 respectively.

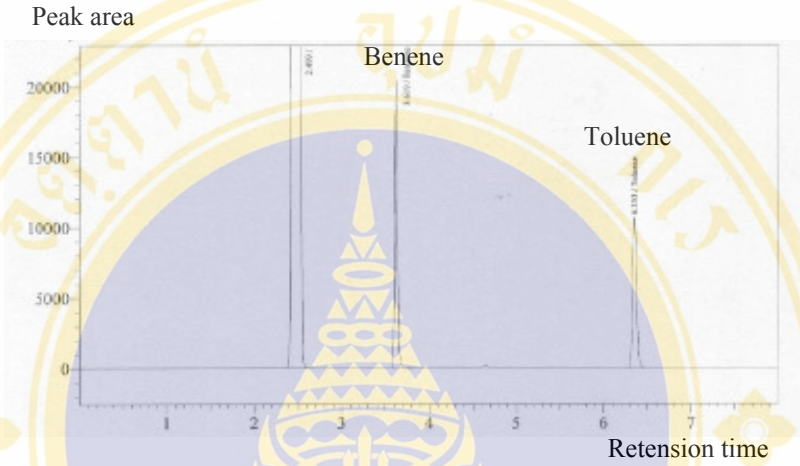

Fig. 4 Chromatograms of standard sample

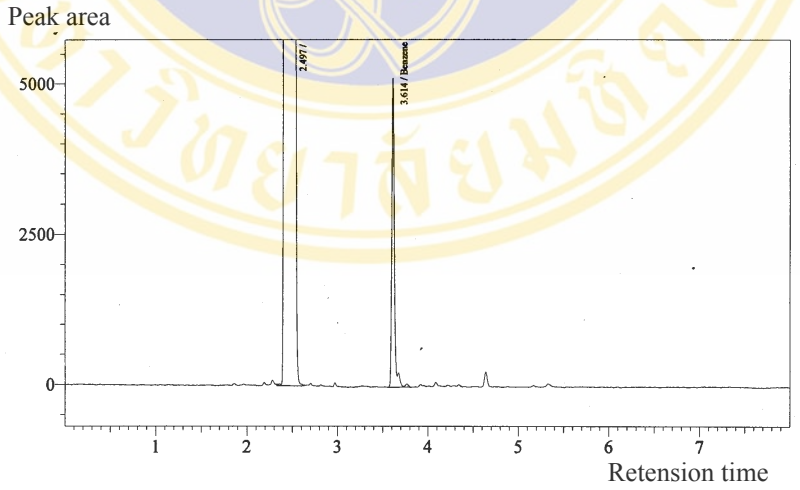

Fig 5 Chromatograms of pure carbon disulfide

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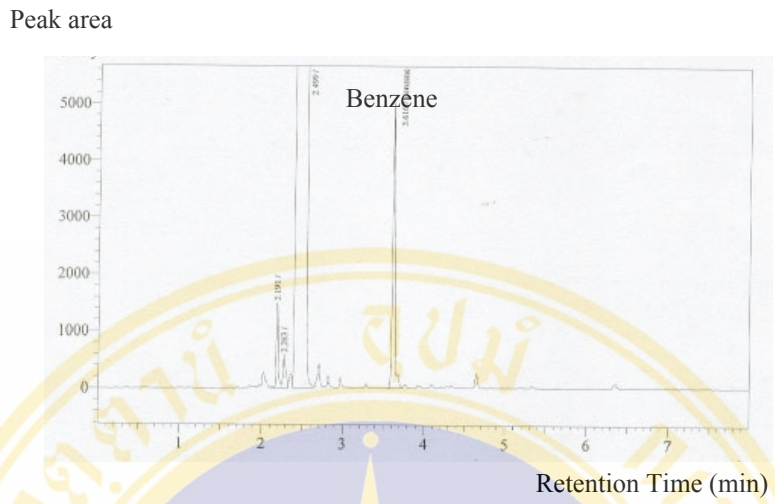

Fig. 6 Chromatograms of blank sample

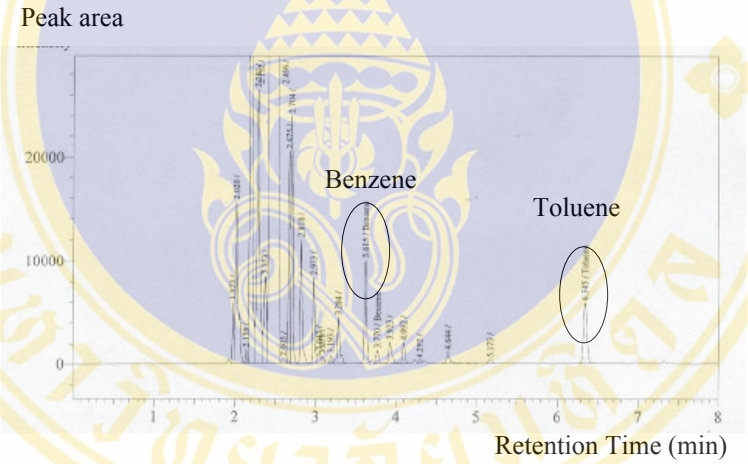

Fig. 7 Chromatograms of air sample at breathing zone of subjects

4.1.2 Chromatogram of benzene and toluene concentrations in gasoline

The chromatograms of benzene and toluene concentrations which used as standard sample showing benzene and toluene peak separated at the retention time of 4.87 and 8.60 min, respectively (Fig 8). Chromatograms of pure carbon disulfide (Analysis Grade) have an unknown peak which has a retention time at 4.865 min (Fig.9)

Chromatogram of benzene and toluene in gasoline is also presented in Fig.10. The retention time of benzene and toluene in gasoline was 4.87 and 8.60 min,

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respectively. There were a lot of interference peaks on the chromatogram, but these two chemicals were resolved from the other peaks

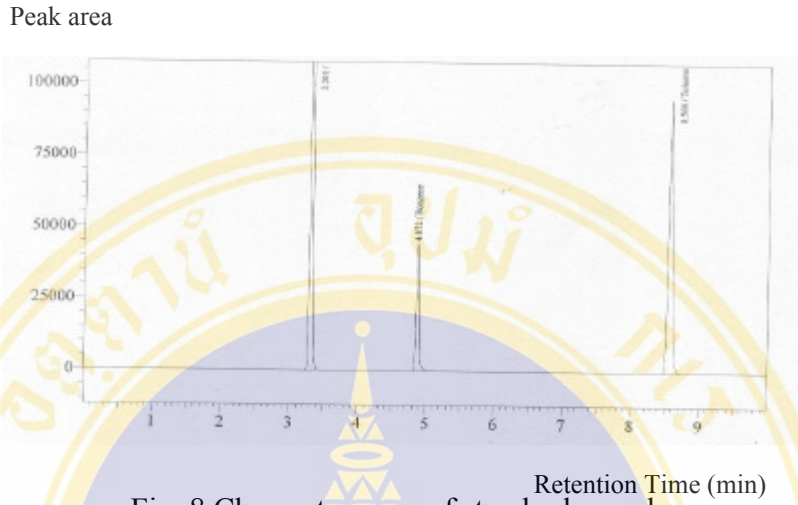

Fig. 8 Chromatograms of standard sample

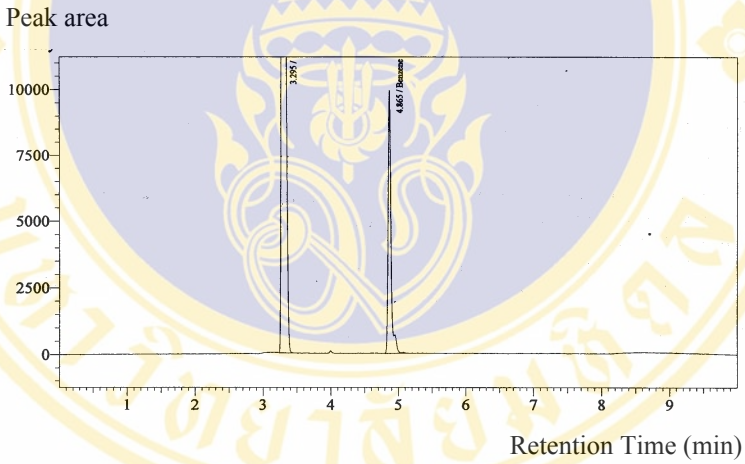

Fig 9 Chromatograms of CS_2 sample

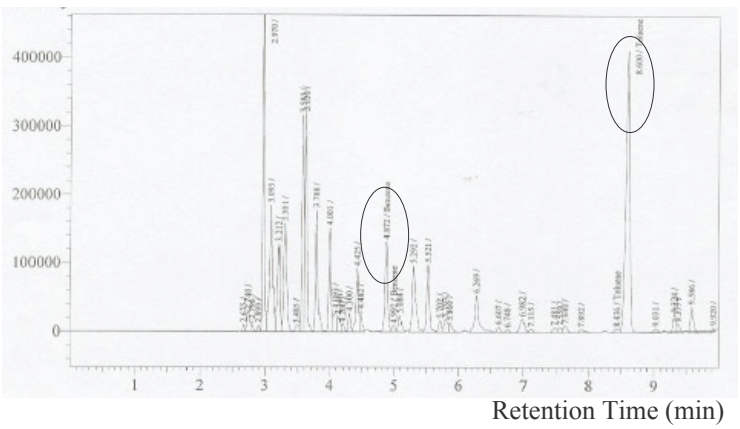

Fig. 10 Chromatograms of gasoline sample

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4.2 Calibration curve for determination of benzene and toluene in air and gasoline

The calibration curves of benzene and toluene showed a linear relationship between the peak area of chemicals and chemical concentrations in air and gasoline The correlation coefficient of calibration curve of benzene and toluene in air was 0.9993, 0.9994 respectively (Fig. 11), and the correlation coefficient of calibration curve of benzene and toluene in gasoline was 0.9969, 0.9991 respectively (Fig. 12).

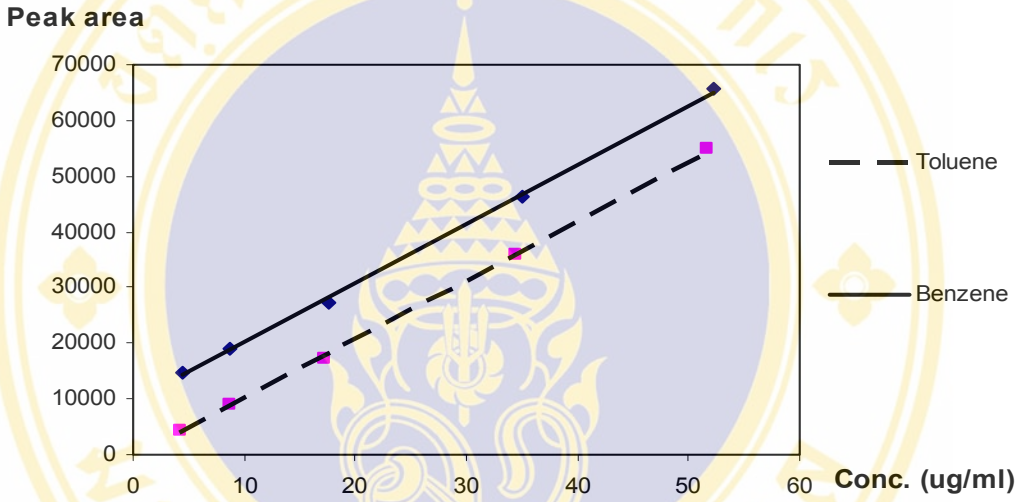

Fig. 11 The calibration curve of benzene and toluene concentration in air

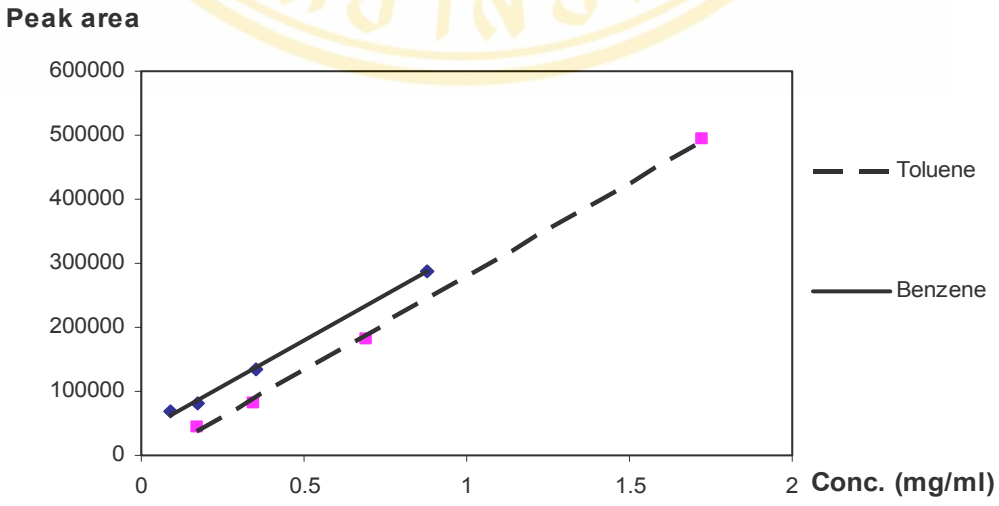

Fig. 12 The calibration curve of benzene and toluene quantity in gasoline

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4.3 Desorption efficiency of benzene and toluene from charcoal

The desorption efficiency of toluene and benzene from charcoal was plotted against the concentrations of benzene and toluene spiked onto the charcoal Fig. 13 and 14, respectively. The desorption curve of benzene represented by the equation of $y = 2.77216 \ln(x) + 64.736$ with $r^2 = 0.9357$, when y = desorption efficiency (%) and x = benzene concentration (µg). In addition, The desorption curve of toluene represented by the equation of $y = 4.7677 \ln(x) + 80.093$ with $r^2 = 0.872$., when y = desorption efficiency and x = toluene concentration (µg). These desorption efficiency curves ware used for calculation of corrected mass of benzene and toluene in air.

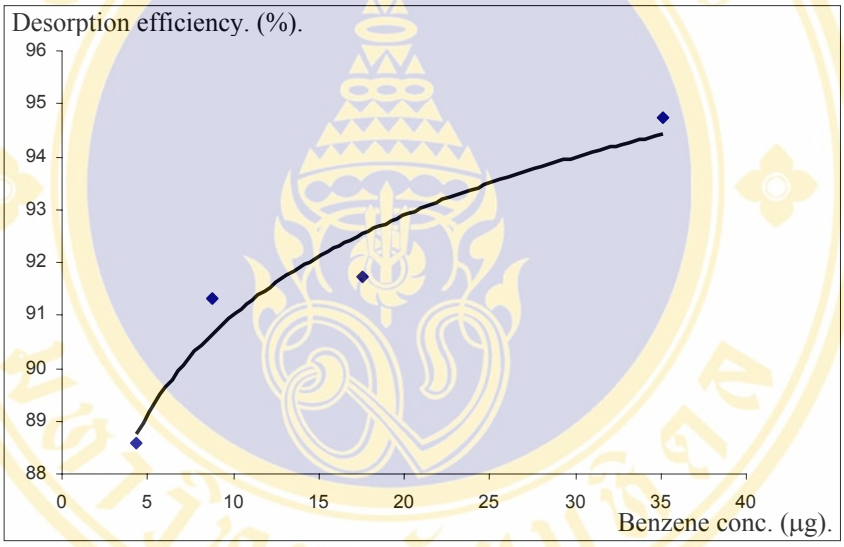

Fig. 13 The desorption curve of benzene

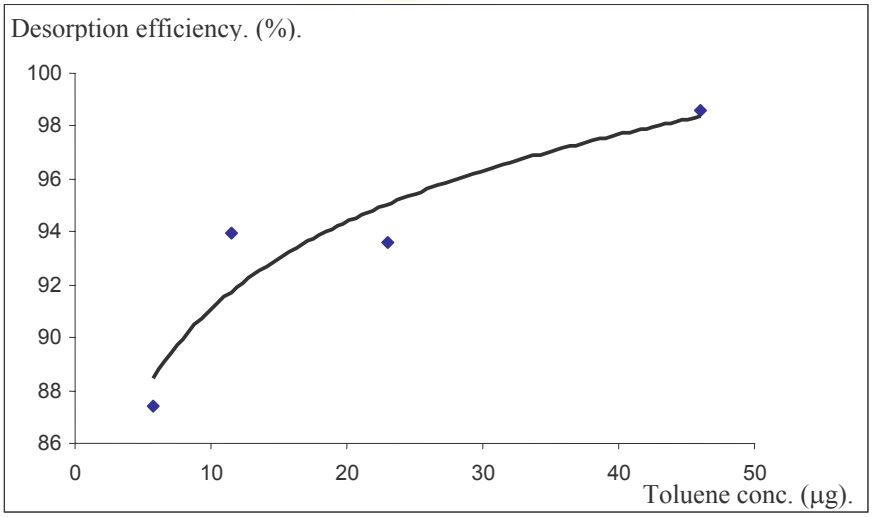

Fig. 14 The desorption curve of toluene

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4.4 The general characteristics of subjects

This study was conducted at 46 gasoline service stations located in Bangkok and boundary area. The number of service station and attendants are shown in table 5. The three brands of gasoline service stations were collected, 46 stations and 165 subjects altogether. Of these, 30 stations (65.22%) and 108 subjects (65.45) were collected from brand A; 11 stations (23.91%) and 44 subjects (26.67%) from brand B, and 5 stations (10.87%) and 13 subjects (7.88%) from brand C.

Table 5 Number of gasoline service stations and subjects

Brand	Service station		Subject	
	Number	Percent	Number	Percent
A	30	65.22	107	64.85
B	11	23.91	45	27.27
C	5	10.87	13	7.88
Total	46	100.00	165	100.00

The general characteristics of service station attendants of this research are shown in table 6. These factors were sex, age, height and smoking habit of subject. Most of the gasoline service station attendants were male (69.94%). Age of subject ranged from 16 to 42; half of them were under 20 years old (51.59%). 40.13% of subjects were 21-30 years old, and 8.28% were more than 30 years old. The subject height was 145-178 centimeters; 44.94% of subjects were lower than 160 cm.; 43.67% ranging from 161 to170 cm and 11.39% were over 170 cm. Most of service station attendants were non smoking (63.03%), and subject who smoking found average number of cigarette smoking per day was 3.31 ± 1.70.

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Table 6 The general characteristics of service station attendants

Characteristics	n	%	Mean±SD	range
Sex				
Male	114	69.94		
Female	49	30.06		
Total	163	100.00		
Age (years)				
≤20	81	51.59		
21-30	63	40.13		
>30	13	8.28		
Total	157	100.00	21.94±5.53	16-42
Height (cm.)				
≤160	71	44.94		
161-170	69	43.67		
>170	18	11.39		
Total	158	100.00	162.80±7.39	145-178
Smoking				
Non smoking	104	63.03		
Smoking	61	36.97		
Total	165	100.00	1.22±1.90	0-8
No. of cigarettes smoked/day	-	-	3.31±1.70	1-8

Regarding environmental conditions of service stations, average humidity was 57.10±7.37% ranging from 41.03 to 76.05; average temperature of 32.46±1.57°C with a range of 26.37-34.81 °C (table 7). For wind speed, it ranged from 0.53 to 1.77 with mean of 0.92±0.30 m/s. Concerning benzene and toluene concentration in gasoline, gasoline 91 from these 3 brands contained 1.70±0.49 %(v/v) benzene, ranging 0.79-2.69% and 7.23±2.47%(v/v) toluene, ranging 2.96-18.52 while gasoline 95 contained 1.56±0.41%(v/v) benzene, ranging 0.72 to 2.46 and 7.02±1.78 %(v/v) toluene, ranging 2.85 – 11.27. The average amount of gasoline sold on the day of data collection was 7482.36±4765.75 liter and range from 421 to 19,164 liters.

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Table 7 Factor of gasoline service stations

Factor	n	Mean ±S.D.	Minimum	Maximum
Environmental Factors				
Humidity (%)	46	57.10±7.37	41.03	76.05
Temperature (°C)	46	32.46±1.57	26.37	34.81
Wind speed (m/s)	46	0.92±0.30	0.53	1.77
Benzene in gasoline				
91 (%vol)	46	1.70±0.49	0.79	2.69
95 (%vol)	46	1.56±0.41	0.72	2.46
Toluene in gasoline				
91 (%vol)	46	7.23±2.47	2.96	18.52
95 (%vol)	46	7.02±1.78	2.85	11.27
Amount of gasoline sold (liter)	45	7482.36±4765.75	421	19,164

4.5 Benzene and toluene concentrations in gasoline and in breathing zone air.

4.5.1 Benzene concentrations in gasoline 91 and 95

Comparison of gasoline 91 among three brands studied, the results showed that the concentrations of benzene in these three brands were significantly different at $p \leq 0.001$. It means that each company may receive gasoline from different refinery plant, and different source of crude oil. Brand B had highest benzene concentration while brand A had lowest concentration (table 8).

With regards to gasoline 95, concentrations of benzene in gasoline for brand A and C were not significantly different, but they were significantly different from brand

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B at $p < 0.001$. Brand B had highest benzene concentration. At present, government regulation stated that the benzene concentration in gasoline should not more than 3.5%. Therefore, these three companies were compliance with the government standard.

Table 8 Percent by volume of benzene in gasoline 91 and 95 for each brand

Brand	n	Benzene in gasoline (% by volume)		P-value
		Mean	SD	
Gasoline 91				
A	30	1.4247	0.3204	< 0.001
B	11	2.3273	0.2356	
C	5	1.7182	0.2115	
Total	46	1.6885	0.4901	
Gasoline 95				
A	30	1.4049	0.3589	< 0.001
B	11	1.9462	0.2965	
C	5	1.4537	0.1118	
Total	46	1.5531	0.4058	

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4.5.2 Toluene concentrations in gasoline 91 and 95

A comparison of toluene in gasoline 91 among three brands studied, the results showed that the toluene concentrations in these three brands were significantly different at $p \leq 0.001$. Brand C had highest toluene concentration while brand A had lowest concentration.

With regards to gasoline 95, toluene concentrations in gasoline for three brands studied, the results showed that the toluene concentrations in these three brands were significantly different at $p \leq 0.001$; Brand C had highest toluene concentration while brand A had lowest concentration (table 9).

Table 9 Percent by Volume of toluene in gasoline 91 and 95 for each brand

Brand	n	Toluene in gasoline (% by volume)		P-value
		Mean	SD	
Gasoline 91				
A	30	5.84	1.24	< 0.001
B	11	9.01	0.90	
C	5	12.51	2.75	
Total	46	7.23	2.47	
Gasoline 95				
A	30	6.20	1.50	< 0.001
B	11	8.24	1.00	
C	5	9.52	1.05	
Total	46	7.01	1.78	

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4.5.3 Benzene and toluene concentrations in breathing zone air

The results of benzene exposure of service station attendants collected from 165 subjects in 46 gasoline service stations were summarized in table 6. The average atmospheric benzene and toluene concentrations were 54.48 ± 30.16 and 78.63 ± 38.02 ppb, respectively. A comparison among the three brands collected, the average atmospheric benzene and toluene concentrations from these three brands were significantly different at $p = 0.027$ and $p < 0.01$, respectively. (Table 10 and 11)

Table 10 Benzene concentration in atmospheric each brand

Brand	n	Atmospheric Benzene Concentration (ppb)		P-value
		Mean	SD	
A	107	49.0116	25.8491	0.027*
B	45	66.1598	38.2971	
C	13	59.0680	18.6297	
Total	165	54.4807	30.1558	

Table 11 Toluene concentration in atmospheric each brand

Brand	n	Atmospheric Toluene Concentration (ppb)		P-value
		Mean	SD	
A	107	68.5639	31.2442	<0.001**
B	45	90.9813	42.6576	
C	13	118.7177	35.2268	
Total	165	78.6293	38.0173	

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4.6 Comparison of atmospheric benzene and toluene exposure at different factors of gasoline service stations.

4.6.1 Comparison of atmospheric benzene concentrations at different benzene concentrations in gasoline octane 91 and 95

The benzene in gasoline evaporates while filling gasoline into the vehicles. In western countries, benzene concentration in gasoline was controlled at 1% following the government regulation, but Thai regulation stated that the benzene concentration should be less than 3.5 %. When comparing the atmospheric benzene concentrations between benzene ≤1% and >1% in gasoline, the result indicated that average atmospheric benzene with benzene >1% was considerably higher than that with benzene ≤1% in gasoline (Table 12). Once again, the gasoline octane 95 also gave the same trend of higher atmospheric benzene at higher %benzene in gasoline.

Table 12 Comparison of atmospheric benzene concentrations at different benzene concentrations in gasoline octane 91 and 95

	n	Atmospheric Benzene Concentration (ppb)		P-value
		Mean	SD	
Benzene in gasoline 91				
≤1%	13	37.2618	19.9656	0.026
>1%	152	55.9534	30.4676	
Benzene in gasoline 95				
≤1%	26	40.9076	25.2920	0.007
>1%	139	57.0195	30.3910	

4.6.2 Comparison of atmospheric benzene and toluene concentrations at different quantity of gasoline sold

Usually, the higher the quantity of gasoline sold, the higher atmospheric benzene and toluene concentration at the breathing zone of station attendants will be.

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The result showed that quantity of gasoline sold at ≤5000, 5001-10000 and >10000 lit gave average atmospheric benzene concentration at 42.78 ± 27.37, 59.83 ± 30.18, and 64.37 ± 29.03 ppb, respectively, toluene concentration at 68.34 ± 38.93, 79.91 ± 34.95, and 91.42 ± 36.88ppb, respectively. The result clearly showed that atmospheric benzene and toluene concentration increased with the increasing quantity of gasoline sold. When comparing quantity of gasoline sold at ≤5000, 5001-10000 and >10000 lit, atmospheric benzene concentrations were significantly different at 95% confidence interval but atmospheric toluene concentrations were not significantly different. (Table 13 and table 14).

Table 13 Comparison of atmospheric benzene concentrations at different quantity of gasoline sold

Quantity of gasoline sold (L)	n	Atmospheric Benzene Concentration (ppb)		P-value
		Mean	SD	
≤5000	64	42.78	27.37	<0.001
5001-10000	55	59.83	30.18	
>10000	46	64.37	29.03	
Total	165	54.48	30.16	

Table 14 Comparison of atmospheric toluene concentrations at different quantity of gasoline sold

Quantity of gasoline sold (L)	n	Atmospheric Toluene Concentration (ppb)		P-value
		Mean	SD	
≤5000	64	68.34	38.93	0.006
5001-10000	55	79.91	34.95	
>10000	46	91.42	36.88	
Total	165	78.6293	38.0173	

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4.6.3 Comparison of atmospheric benzene concentrations at different environmental conditions

The several environmental conditions of gasoline service station were monitored, such as relative humidity, temperature and wind speed. Only the relative humidity gave significant relationship with atmospheric benzene and toluene concentration. The result showed that the relative humidity ≤ 60% and >60 % gave significant different atmospheric benzene concentration at 95% confidence interval. It means that at higher relative humidity, the atmospheric benzene and toluene concentration were reduced. (Table 15 and table 16)

Table 15 Comparison of atmospheric benzene concentrations at different environmental conditions

Relative humidity (%)	n	Atmospheric Benzene Concentration (ppb)		P-value
		Mean	SD	
≤ 60%	118	56.6772	27.2535	0.015
> 60%	47	48.9661	36.1866	
Total	165	54.4807	30.1558	

Table 16 Comparison of atmospheric toluene concentrations at different environmental conditions

Relative humidity (%)	n	Atmospheric Toluene Concentration (ppb)		P-value
		Mean	SD	
≤ 60%	118	82.5874	35.2994	0.002
> 60%	47	68.6918	42.9242	
Total	165	78.6293	38.0173	

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4.7 The benzene exposure estimated model of station attendants.

Due to the wide variation of atmospheric benzene concentrations in the same service station, the researcher decided to average atmospheric benzene concentration in each station to represent atmospheric benzene exposure of service attendants in each station. The quantity of gasoline sold was missing for one service station; therefore, 45 service stations (3 gasoline service companies) were used for the benzene exposure estimated model of station attendants.

4.7.1 Correlation of atmospheric benzene concentration with other factors for 3 gasoline service companies

The correlation of atmospheric benzene concentration was carried out for 3 gasoline service companies with a total of 45 service stations. The factors that have significant relationship with atmospheric benzene concentration were quantity of gasoline sold each day($r = 0.462$; p-value = 0.01), benzene concentration in gasoline octane 91 ($r = 0.139$; p-value = 0.033), and benzene concentration in gasoline octane 95 ($r = 0.548$; p-value ≤ 0.01), (Table 17).

Table 17 Correlation of atmospheric benzene concentration with other factors for 3 gasoline service companies

	Y1	X1	X2	X3	X4	X5	X6
Y1	1.00						
X1	0.462	1.00					
X2	0.139	-0.204	1.00				
X3	0.548	0.067	0.538	1.00			
X4	0.023	-0.002	0.013	-0.042	1.00		
X5	0.057	0.372	-0.061	0.049	-0.057	1.00	
X6	0.12	0.021	-0.010	0.206	-0.008	-0.027	1.00

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Y1 = Atmospheric benzene concentration
X1 = Quantity of gasoline sold
X2 = Benzene in gasoline 91
X3 = Benzene in gasoline 95
X4 = Humidity
X5 = Temperature
X6 = Wind speed

The appropriate estimated model (Table 18 and 19) of atmospheric benzene concentration from these independent variables is Y1 = -17.49 + 2.16X1 + 35.41X3 with r^2 = 0.512 at 95% confident limit, while Y = atmospheric benzene concentration, X1 = quantity of gasoline sold and X3 = benzene concentration in gasoline 95 which was named as model I. It means that the atmospheric benzene concentration can be estimated from model I with 51.2 % accuracy. The atmospheric benzene concentration can be influenced by benzene concentration in gasoline 95 more than quantity of gasoline sold. If a benzene concentration in gasoline 95 increase 1 % without influencing by quantity of gasoline sold, then atmospheric benzene concentration increase at 35.41 ppb.

Table 18 The estimated model of atmospheric benzene concentration from these independent variables for 3 gasoline service companies

Model	R	R Square	F	P-value
I	0.716	0.512	22.071	<0.001

Preditors : (Constant), Benzene in gasoline 95, Quantity of gasoline sold

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Table 19 Coefficients of the estimated model of atmospheric benzene concentration for 3 gasoline service companies

Model	Unstandardized Coefficients		Standardized Coefficients	t	p
	B	S.E.	Beta		
(Constant)	-17.487	11.157		-1.567	0.125
Benzene in Gasoline 95	35.141	6.549	0.579	5.366	<0.001
Quantity of gasoline sold	2.163	0.589	0.396	3.671	0.001

4.7.2 Correlation of atmospheric benzene concentration with other factors for 2 gasoline service companies (A and B)

Owing to lower number of brand C (4 service stations), the correlation of atmospheric benzene concentration was reduced to 2 gasoline service companies with a total of 41 service stations. The factors that have significant relationship with atmospheric benzene concentration were still be quantity of gasoline sold each day ($r = 0.549$; p-value ≤ 0.01), benzene concentration in gasoline octane 91 ($r = 0.327$; p-value $= 0.037$), and benzene concentration in gasoline octane 95 ($r = 0.558$; p-value ≤ 0.01), (Table 20).

Table 20 Correlation of atmospheric benzene concentration with other factors for 2 gasoline service companies (A and B)

	Y1	X1	X2	X3	X4	X5	X6
Y1	1.00						
X1	0.549	1.00					
X2	0.327	-0.116	1.00				
X3	0.558	0.050	0.596	1.00			
X4	0.019	-0.094	0.035	-0.102	1.00		
X5	0.122	0.227*	0.033	0.014	-0.169	1.00	
X6	0.195	0.046	-0.010	0.280	-0.006	-0.048	1.00

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Y1 = Atmospheric benzene concentration
X1 = Quantity of gasoline sold
X2 = Benzene in gasoline 91
X3 = Benzene in gasoline 95
X4 = Humidity
X5 = Temperature
X6 = Wind speed

The appropriate estimated model of atmospheric benzene concentration from these independent variables of model II is Y1 = -23.07 + 2.58X1 + 35.82X3 with r^2 = 0.547 at 95% confident limit, while Y1 = atmospheric benzene concentration, X3 = benzene concentration in gasoline 95 and X1 = quantity of gasoline sold. It means that the atmospheric benzene concentration can be estimated from this model with 54.7 % accuracy. The atmospheric benzene concentration can be influenced by benzene concentration in gasoline 95 more than quantity of gasoline sold. If a benzene concentration in gasoline 95 increase 1 % without influencing by quantity of gasoline sold, then atmospheric benzene concentration increase at 35.82 ppb. After excluding four service station of company C, the correlation coefficient of the estimated atmospheric benzene concentration model slightly increases. (Table 21 and 22)

Table 21 The estimated model of atmospheric benzene concentration from these independent variables for 2 gasoline service companies (A&B)

Model	R	R Square	F	P-value
II	0.740	0.547	22.981	<0.001

Preditors : (Constant), Benzene in gasoline 95, Quantity of gasoline sold

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Table 22 Coefficients of the estimated model of atmospheric benzene concentration for 2 gasoline service companies (A&B)

Model	Unstandardized Coefficients		Standardized Coefficients	t	p
	B	S.E.	Beta		
(Constant)	-23.066	11.818		-1.952	0.058
Benzene in Gasoline 95	35.815	6.877	0.569	5.208	<0.001
Quantity of gasoline sold	2.577	0.636	0.443	4.051	<0.001

The summary of the appropriate estimated models of atmospheric benzene concentration from these independent variables is presented in table 23. The result clearly indicated that all these appropriate estimated models of atmospheric benzene concentration can be used to predict the atmospheric benzene concentration in gasoline service stations in order to plan for reducing benzene exposure in service attendants. The major factors influencing the atmospheric benzene concentration are quantity of benzene in gasoline, quantity of gasoline sold and relative humidity. The most influencing factor of atmospheric benzene concentration is quantity of benzene in gasoline; therefore, reducing of quantity of benzene in gasoline should be implemented to reduce atmospheric benzene exposure in gasoline service attendants.

Table 23 Summary of the appropriate estimated model of atmospheric benzene concentration from these independent variables.

	Model	R	R Square	Equation	P-value
I	3 companies	0.716	0.512	Y1 = -17.49 + 2.16X1 + 35.41X3	<0.001
II	2 companies (A&B)	0.740	0.547	Y1 = -23.07 + 2.58X1 + 35.82X3	<0.001

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4.8 The Toluene exposure estimated model of station attendants.

Due to the wide variation of atmospheric toluene concentrations in the same service station, the researcher resolute to average atmospheric toluene concentration in each station to represent atmospheric toluene exposure of service attendants in each station. The quantity of gasoline sold was missing for one service station; therefore, 45 service stations (3 gasoline service companies) were used for the toluene exposure estimated model of station attendants.

4.8.1 Correlation of atmospheric toluene concentration with other factors for 3 gasoline service companies

The correlation of atmospheric toluene concentration was carried out for 3 gasoline service companies with a total of 45 service stations. The factors that have significant relationship with atmospheric toluene concentration were toluene concentration in gasoline octane 91 ($r = 0.560$; p-value ≤ 0.001), and toluene concentration in gasoline 95 ($r = 0.666$; p-value ≤ 0.001), (Table 24).

Table 24 Correlation of atmospheric toluene concentration with other factors for 3 gasoline service company

	Y2	X1	Z1	Z2	X4	X5	X6
Y2	1.00						
X1	0.251	1.00					
Z1	0.560	-0.216	1.00				
Z2	0.666	-0.170	0.796	1.00			
X4	-0.266	-0.131	0.042	0.017	1.00		
X5	0.066	0.414	-0.229	-0.208	-0.418	1.00	
X6	-0.106	-0.206	0.031	0.146	0.050	-0.027	1.00

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Y2 = Atmospheric toluene concentration
X1 = Quantity of gasoline sold
Z1 = Toluene in gasoline 91
Z2 = Toluene in gasoline 95
X4 = Humidity
X5 = Temperature
X6 = Wind speed

The appropriate estimated model III of atmospheric toluene concentration from these independent variables (Table 25 and 26) is Y2 = -14.634 + 11.238Z2 with r^2 = 0.515 at 99% confident limit, while Y2 = atmospheric toluene concentration and Z2 = Toluene in gasoline octane 95. It means that the atmospheric benzene concentration can be estimated from this model with 51.5 % accuracy. If a toluene concentration in gasoline octane 95 increases 1 % without influencing by quantity of gasoline sold, then atmospheric benzene concentration will increase at 11.238 ppb.

Table 25 The estimated model of atmospheric toluene concentration from these independent variables for 3 gasoline service companies

Model	R	R Square	F	P-value
III	0.718[b]	0.515	22.317	<0.001

Preditors : (Constant), Toluene in gasoline 95 and quantity of gasoline sold

Table 26 Coefficients of the estimated model of atmospheric toluene concentration for 3 gasoline service companies

Model	Unstandardized Coefficients		Standardized Coefficients	t	P-value
	B	S.E.	Beta		
(Constant)	-14.634	14.329		-1.021	0.313
Toluene in gasoline 95	11.238	1.761	0.690	6.381	<0.001
Quantity of gasoline sold	1.97×10^{-3}	0.001	0.292	2.696	0.10

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4.8.2 Correlation of atmospheric toluene concentration with other factors for 2 gasoline service companies (A&B)

With regards to company A&B, there were 41 service stations including in the analysis. Certainly, the factors that have significant relationship with atmospheric toluene concentration were still be quantity of gasoline sold each day ($r = 0.487$; p-value = 0.01), toluene concentration in gasoline octane 91 ($r = 0.466$; p-value =0.002), and toluene concentration in gasoline 95 ($r = 0.602$; p-value = <0.001), and temperate ($r = 0.6321$; p-value = 0.041), (Table 27).

Table 27 Correlation of atmospheric toluene concentration with other factors for A&B gasoline service companies

	Y2	X1	Z1	Z2	X4	X5	X6
Y2	1.00						
X1	0.487**	1.00					
Z1	0.466**	-0.001	1.00				
Z2	0.602**	0.021	0.747**	1.00			
X4	-0.217	-0.288*	0.207	0.144	1.00		
X5	0.321*	0.268	0.018	0.011	-0.672**	1.00	
X6	-0.063	-0.205	0.063	0.184	0.015	-0.048	1.00

Y2 = Atmospheric toluene concentration
X1 = Quantity of gasoline sold
Z1 = Toluene in gasoline 91
Z2 = Toluene in gasoline 95
X4 = Humidity
X5 = Temperature
X6 = Wind speed

The appropriate estimated model IV of atmospheric toluene concentration from these independent variables is $Y2 = -13.17 + 10.276Z2 + 2.43x10^{-3}X1$ with $r^2 = 0.529$ at 95% confident limit, while Y2 = atmospheric toluene concentration, X1 = quantity

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of gasoline sold and Z2 = Toluene in gasoline 95 (Table 28 and 29). It means that the atmospheric toluene concentration can be estimated from this model with 52.9% accuracy. The atmospheric toluene concentration can be influenced by toluene concentration in gasoline 95 much more than quantity of gasoline sold. If a toluene concentration in gasoline 95 increases 1 % without influencing by quantity of gasoline sold, then atmospheric benzene concentration will increase at 10.276 ppb.

Table 28 The estimated model of atmospheric toluene concentration from these independent variables for 3 gasoline service companies

Model	R	R Square	F	P-value
IV	0.727[b]	0.529	21.354	<0.001

Preditors : (Constant), Toluene in gasoline 95, Quantity of gasoline sold

Table 29 Coefficients of the estimated model of atmospheric toluene concentration for 3 gasoline service companies

Model	Unstandardized Coefficients		Standardized Coefficients	t	P-value
	B	S.E.	Beta		
(Constant)	-13.170	14.038		-0.938	0.354
Toluene in Gasoline 95	10.276	1.892	0.605	5.430	<0.001
Quantity of gasoline sold	$2.43x10^{-3}$	0.001	0.370	3.318	0.002

The summary of the appropriate estimated models of atmospheric toluene concentration from these independent variables is presented in table 30. The result indicated that all these appropriate estimated models of atmospheric toluene concentration can be used to predict the atmospheric toluene concentration in gasoline service stations in order to plan for reducing toluene exposure in service attendants. The major factors influencing the atmospheric toluene concentration are quantity of toluene in gasoline, and quantity of gasoline sold. The most influencing factor of atmospheric toluene concentration is quantity of toluene in gasoline; therefore,

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reducing of quantity of toluene in gasoline should be implemented to reduce atmospheric toluene exposure in gasoline service attendants.

Table 30 Summary of the appropriate estimated model of atmospheric toluene concentration from these independent variables

	Model	R	R Square	Equation	P-value
III	3 companies	0.718	0.515	$Y2 = -14.634 + 11.238Z2$	<0.001
IV	2 companies (A&B)	0.727	0.529	$Y2 = -13.17 + 10.276Z2 + 2.43x10^{-3}X1$	<0.001

The estimated atmospheric benzene exposure model in this study can be summarized into 2 models with little different r^2:

For three company, Model I : $Y1 = -17.49 + 2.16X1 + 35.41X3$, $r^2 = 0.512$

For company A and B, Model II : $Y1 = -23.07 + 2.58X1 + 35.82X3$, $r^2 = 0.547$

For the estimated atmospheric toluene exposure model in this research can be summarized into 2 models therefore;

For three companies, Model III : $Y2 = -14.634 + 11.238Z2$, $r^2 = 0.515$

For company A and B, Model IV : $Y2 = -13.17 + 10.276Z2 + 2.43x10^{-3}X1$, $r^2 = 0.529$

While, Y1 = Atmospheric benzene concentration

Y2= Atmospheric toluene concentration

X1 = Quantity of gasoline sold

X3 = Benzene in gasoline 95

Z2 = Toluene in gasoline 95

All models, factors which have affect benzene and toluene exposure are the same factors, but r^2 of all models is little different. Thus Model II is the best model to use for prediction of benzene exposure because r^2 is highest.

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CHAPTER V
DISCUSSION

5.1 Chromatogram of benzene and toluene in air and gasoline

The result showed that there was a peak of other chemical having the same retention time as the benzene peak in the blank. It has been proved that the peak having the same retention time with benzene came from impurity in carbon disulfide which was used as solvent for desorption. However, the quantity of benzene in the blank was approximately 0.2-0.3 μg considered a trace amount of benzene.

The pattern of chemicals found on the chromatogram of benzene in air and in gasoline was similar. There were a lot chemicals found on the chromatogram of benzene in air and in gasoline, but the benzene and toluene peak were resolved within 10 min but still a lot of time spent for eluting all the chemicals from the column for each analysis.

5.2 Desorption efficiency of benzene and toluene from charcoal

The desorption efficiency of benzene and toluene from charcoal was greater than 85%; therefore, it follows NIOSH criteria. The desorption efficiency was very important in determining the corrected mass of benzene and toluene in air after desorbing from charcoal. It seem that the desorption efficiency curve was not so good because the trend line could not pass through all the points tested for both benzene and toluene desorption curves.

5.3 The characteristics of gasoline service stations and service station attendants

5.3.1 General characteristic of subjects

The experimental design intended to collect the same amount of samples from these three brands. At the beginning of sample collection, the government promoted

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the use of gasohol to replace gasoline. Brand B and C had started selling gasohol during that period. The number of service stations of brand B and C was reduced, because the researcher decided to collect samples in service station without gasohol.

Most of service attendants were male because their shift was ranged from 8 to12 hr. They had to work for 8 to 12 hr a day. There was only a few service station had a shift of 8 hr. Most of them (91%) were ≤ 30 years old. They were very active while working and had to expose to benzene in air for all workdays. Some of them (36.97%) smoked cigarettes, although they were not allowed to smoke while working. Usually, smoking cigarette also added benzene and toluene exposure to subjects.

5.3.2 Factors of gasoline service stations, i.e. environmental conditions, amount of gasoline sold and benzene content in gasoline.

Generally, environmental conditions of service stations may have an influence on benzene and toluene exposure for service attendants. The relative humidity during the period of sample collection was very wide ranging from 41.03 to 76.05% because it covered from the end of summer to the beginning of rainy season. The temperature range was also wide; the temperature was low (26.37 °C) at rainy season and high at summer season. The wind speed was narrow because the point of sample collection was in between a filling nozzle and a vehicle that blocked the flow of wind, although almost of service stations had good natural ventilation.

With regards to benzene and toluene in gasoline, the result showed that the benzene concentration in gasoline octane 91 was higher than that in gasoline octane 95, while the toluene concentrations for both gasoline octane 91 and 95 was similar.

5.4 Benzene and toluene concentrations in gasoline and in breathing zone air.

5.4.1 Benzene and toluene concentrations in gasoline 91 and 95

The three brands studied had different benzene and toluene concentrations in gasoline 91 and 95 probably due to source of crude oil, refinery process and technology of oil refinery. The station distributed gasoline with low benzene and toluene content received gasoline from high technology oil refinery company.

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5.4.2 Benzene and toluene concentrations in breathing zone air

The average benzene and toluene concentrations in breathing zone air of service attendants from these three brands studied were significantly different at p =0.05 and p = 0.01, respectively probably due to the different benzene and toluene content in gasoline. The average benzene concentrations from this study was 54.48 ± 30.15 ppb which was considered lower than the level (64.78 ±17.59 ppb) studied by Navasumrit, P and et al.(2005). It may be because this study used charcoal tube (400/200 mg charcoal) and collecting air sample for full shift (8- to 12-hr sample collection), but the study by Navasumrit, P and et al. used diffusive badge (3M organic vapor monitor 3500) and collecting sample for 8-hr. The study of Foo, S.-C. (1991) found time-weighted average of benzene exposure for service station attendant of 0.028-0.71 ppm which was higher than the result of this study. It was probably because the study of Foo, S.-C. had higher benzene concentration (1.8-3.7%) in gasoline.

5.5 Comparison of atmospheric benzene and toluene exposure and factors of gasoline service stations.

5.5.1 Comparison of atmospheric benzene concentration and gasoline octane 91 and 95

The result showed that the atmospheric benzene concentration had significant relationship with the benzene concentration in gasoline. If the government reduces the benzene concentration in gasoline, then the atmospheric benzene concentration will be reduced. At present time, the government promoted the use of gasohol, ethyl alcohol was used to mix with gasoline at 10%. Then, the benzene content in gasoline was reduced for only 0.1%. Since, benzene has been proofed to be a confirmed human carcinogen; the use of benzene should be reduced to a minimum. The alternative way to reduce benzene exposure for service attendants is to reduce the benzene concentration in gasoline.

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5.5.2 Comparison of atmospheric benzene and toluene concentrations at different quantity of gasoline sold

The result clearly stated that atmospheric benzene and toluene concentration increased with the increasing quantity of gasoline sold. One alternate way to reduce atmospheric benzene and toluene exposure of service attendants is to promulgate the use of vapor recovery at the service station and design the working environment of service station with better ventilation.

5.5.3 Comparison of atmospheric benzene and toluene concentrations at different environmental conditions

The result showed that at higher relative humidity, the atmospheric benzene concentration was reduced , because the water vapour in atmosphere reduce the evaporation rate of benzene. The temperature and wind speed did not change much during the period of sampling collection; therefore, they did not have an effect on atmospheric benzene and toluene concentrations.

5.6 The benzene and toluene exposure estimated model of station attendants.

The estimated atmospheric benzene exposure model in this study can be summarized into 2 models with little different r^2:

For three company, Model I : $Y1 = -17.49 + 2.16X1 + 35.41X3$, $r^2 = 0.512$

For company A and B, Model II : $Y1 = -23.07 + 2.58X1 + 35.82X3$, $r^2 = 0.547$

For the estimated atmospheric toluene exposure model in this research can be summarized into 2 models therefore;

For three companies, Model III : $Y2 = -14.634 + 11.238Z2$, $r^2 = 0.515$

For company A and B, Model IV : $Y2 = -13.17 + 10.276Z2 + 2.43x10^{-3}X1$, $r^2 = 0.529$

While, Y1 = Atmospheric benzene concentration

Y2= Atmospheric toluene concentration

X1 = Quantity of gasoline sold

X3 = Benzene in gasoline 95

Z2 = Toluene in gasoline 95

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All models, factors which have affect benzene and toluene exposure are the same factors, but r^2 of all models is little different. Thus Model II is the best model to use for prediction of benzene exposure because r^2 is highest.

The most influencing factor of atmospheric benzene and toluene concentrations is quantity of benzene in gasoline; therefore, reducing of quantity of benzene and toluene in gasoline should be implemented to reduce atmospheric benzene and toluene exposure of gasoline service attendants. Supposing Thai government reduces the quantity of benzene in gasoline from 3.5% down to 1%, without the effect of quantity of gasoline sold and other factor, the atmospheric benzene and toluene exposure of gasoline service attendants will be considerably reduced. In this research with model I, the maximum quantity of benzene in gasoline 95 was 2.46% producing atmospheric benzene concentration of 63.84 ppb. If the quantity of benzene in gasoline 95 is reduced to 1%, then the atmospheric benzene exposure of gasoline service attendants will be 46.42% reduction to a level of 34.21 ppb. Supposing Thai government reduces the quantity of benzene in gasoline from 3.5% down to 1%, using model II, the atmospheric benzene concentration will be reduced from 63.84 ppb to 23.99 ppb with 53.58 % reduction. Thai government should considered reducing the quantity of benzene in gasoline to protect service station workers' health and to conserve overall natural environment

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CHAPTER VI
CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The predicted model of atmospheric benzene exposure among service attendants was carried out in 46 service station attendants, 165 service attendants. The result produced 2 appropriate models for prediction of atmospheric benzene exposure and 2 models for atmospheric toluene exposure among service attendants as follow:

1. Model I : $Y1 = -17.49 + 2.16X1 + 35.41X3$, $r^2 = 0.512$
2. Model II : $Y1 = -23.07 + 2.58X1 + 35.82X3$, $r^2 = 0.547$
3. Model III : $Y2 = -14.634 + 11.238Z2$, $r^2 = 0.515$
4. Model IV : $Y2 = -13.17 + 10.276Z2 + 2.43 \times 10^{-3}X1$, $r^2 = 0.529$

where;

Y1 = Atmospheric benzene concentration

Y2 = Atmospheric toluene concentration

X1 = Quantity of gasoline sold

X3 = Benzene in gasoline 95

Z2 = Toluene in gasoline 95

All models can predict atmospheric benzene exposure among service attendants with at least 50% accuracy and factors which affect benzene and toluene exposure of service attendants are similar factors, and r^2 of all models is little different. Thus Model II is the best model because r^2 is highest.

All models can be used efficiently for environmental management authority and private organization to setting up plan for atmospheric benzene concentration reduction in petrol station. The reduction of benzene level in gasoline can be an alternative way to reduce benzene exposure concomitantly with an implementation of vapor recovery in the petrol station.

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6.2 Recommendation

The recommendation for further study is as follows:

1. The data collection should be carried out in the same way for every company studied; for example, number of petrol station participated should be similar.
2. The data collection should be done in different season to see seasonal effect.
3. Number of gasoline station should be much more than this study in order to develop predicted model of atmospheric benzene exposure among service attendants.

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APPENDIX

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APPENDIX A

A-1 The analytical results of benzene and toluene concentration in air and in gasoline

Brand	Pump	No. of subject	Benzene in gasoline octane 91(%V)	Toluene in gasoline octane 91 (%V)	Benzene in gasoline octane 95 (%V)	Toluene in gasoline octane 95 (%V)	Benzene concentration in air (ppb)	Toluene concentration in air (ppb)
1	1	1	1.39	5.94	0.96	5.28	18.2	29.19
1	1	2	1.39	5.94	0.96	5.28	33.59	46.6
1	1	3	1.39	5.94	0.96	5.28	25.33	37.01
1	1	4	1.39	5.94	0.96	5.28	34.47	44.78
1	2	1	1.04	5.05	1.58	6.45	33.33	52.02
1	2	2	1.04	5.05	1.58	6.45	42.74	53.05
1	2	3	1.04	5.05	1.58	6.45	48.7	77.53
1	2	4	1.04	5.05	1.58	6.45	67.84	85.68
1	3	1	0.79	2.96	0.77	3.08	35.2	65.44
1	3	2	0.79	2.96	0.77	3.08	13.82	34.62
1	3	3	0.79	2.96	0.77	3.08	21.17	44.69
1	3	4	0.79	2.96	0.77	3.08	17.23	53.12
1	4	1	1.56	6.42	1.65	7.07	70.1	98.88
1	4	2	1.56	6.42	1.65	7.07	60.19	86.23
1	4	3	1.56	6.42	1.65	7.07	99.76	125.24
1	5	1	1.64	6.25	1.29	5.43	60.16	82.17
1	5	2	1.64	6.25	1.29	5.43	39.32	55.5
1	5	3	1.64	6.25	1.29	5.43	13.06	16.74
1	5	4	1.64	6.25	1.29	5.43	56.7	78.07
1	5	5	1.64	6.25	1.29	5.43	61.47	76.09
1	6	1	1.37	6.23	1.82	7.41	32.17	51.2
1	6	2	1.37	6.23	1.82	7.41	75	95.03
1	6	3	1.37	6.23	1.82	7.41	38.29	52.94
1	7	3	1.54	6.45	1.54	7.86	66.67	92.35
1	7	4	1.54	6.45	1.54	7.86	36.43	57.05
1	7	5	1.54	6.45	1.54	7.86	81.39	107.64
1	8	1	1.53	6.66	1.54	7.13	33.88	71.91
1	8	2	1.53	6.66	1.54	7.13	53.49	64.22
1	8	3	1.53	6.66	1.54	7.13	81.36	64.16
1	9	1	1.05	5.46	1.43	7.24	82.95	89.92
1	9	2	1.05	5.46	1.43	7.24	27.96	49.6
1	9	3	1.05	5.46	1.43	7.24	26.08	50.1
1	9	4	1.05	5.46	1.43	7.24	47.21	65.02
1	10	1	0.97	3.84	1.2	4.51	33.82	46.51
1	10	2	0.97	3.84	1.2	4.51	19.22	42.6
1	11	1	1.53	6.33	1.96	8.4	133.5	183.41
1	11	2	1.53	6.33	1.96	8.4	63.97	77.77
1	11	3	1.53	6.33	1.96	8.4	66.81	81.85
1	12	1	1.42	6.17	1.68	7.82	66.45	78.29
1	12	2	1.42	6.17	1.68	7.82	51.93	96.25
1	12	4	1.42	6.17	1.68	7.82	65.25	81.1
1	12	5	1.42	6.17	1.68	7.82	87.89	103.41

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A-1 The analytical results of benzene and toluene concentration in air and in gasoline (Cont.)

Brand	Pump	No. of subject	Benzene in gasoline octane 91(%V)	Toluene in gasoline octane 91 (%V)	Benzene in gasoline octane 95 (%V)	Toluene in gasoline octane 95 (%V)	Benzene concentration in air (ppb)	Toluene concentration in air (ppb)
1	13	1	1.86	6.77	1.99	8.63	48.44	59.84
1	13	2	1.86	6.77	1.99	8.63	25.25	37.01
1	13	3	1.86	6.77	1.99	8.63	62.62	92.08
1	14	1	1.52	6.8	1.67	7.78	28.44	49.9
1	14	2	1.52	6.8	1.67	7.78	45.48	57.31
1	14	3	1.52	6.8	1.67	7.78	24.82	49.72
1	15	1	0.85	3.03	0.72	2.85	46.82	60.13
1	15	2	0.85	3.03	0.72	2.85	14.13	31.67
1	15	3	0.85	3.03	0.72	2.85	50.79	78.3
1	15	4	0.85	3.03	0.72	2.85	40.62	58.75
1	16	1	1.88	7.24	1.7	7.03	86.02	141.32
1	16	2	1.88	7.24	1.7	7.03	53.51	83.11
1	16	3	1.88	7.24	1.7	7.03	59.58	81.16
1	16	4	1.88	7.24	1.7	7.03	73.79	100.7
1	17	1	1.39	5.9	1.83	7.18	38.36	59.67
1	17	2	1.39	5.9	1.83	7.18	34.22	53.47
1	17	3	1.39	5.9	1.83	7.18	52.32	76.57
1	17	4	1.39	5.9	1.83	7.18	101.16	123.78
1	18	1	1.06	3.78	0.75	3.12	22.82	35.49
1	18	2	1.06	3.78	0.75	3.12	34.23	52.16
1	18	3	1.06	3.78	0.75	3.12	7.69	23.26
1	19	1	0.9	3.73	0.97	4.54	73.63	94.28
1	19	3	0.9	3.73	0.97	4.54	67.52	88.27
1	19	4	0.9	3.73	0.97	4.54	50.43	77.93
1	20	1	2.08	7.54	1.56	6.36	78.93	98.65
1	20	2	2.08	7.54	1.56	6.36	67.32	69.01
1	20	3	2.08	7.54	1.56	6.36	20.35	20.36
1	20	4	2.08	7.54	1.56	6.36	52.28	141.27
1	20	5	2.08	7.54	1.56	6.36	58.94	66.99
1	21	1	1.46	6.43	1.86	6.76	43.42	64.49
1	21	2	1.46	6.43	1.86	6.76	49.47	63.81
1	21	3	1.46	6.43	1.86	6.76	34.67	45.07
1	22	1	1.31	5.97	1.49	6.53	11.33	21.23
1	22	2	1.31	5.97	1.49	6.53	5.96	18.64
1	22	3	1.31	5.97	1.49	6.53	10.54	23.88
1	23	1	1.77	7.13	1.3	6.38	56.52	88.91
1	23	2	1.77	7.13	1.3	6.38	33.9	45.99
1	23	3	1.77	7.13	1.3	6.38	37.24	59.31
1	24	1	1.37	4.82	1.43	5.4	36.1	52.85
1	24	2	1.37	4.82	1.43	5.4	25.83	37.49
1	24	3	1.37	4.82	1.43	5.4	74.18	105.99

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A-1 The analytical results of benzene and toluene concentration in air and in gasoline (Cont.)

Brand	Pump	No. of subject	Benzene in gasoline octane 91(%V)	Toluene in gasoline octane 91 (%V)	Benzene in gasoline octane 95 (%V)	Toluene in gasoline octane 95 (%V)	Benzene concentration in air (ppb)	Toluene concentration in air (ppb)
1	25	1	1.46	5.43	1.39	5.67	28.15	38.96
1	25	2	1.46	5.43	1.39	5.67	13.6	21.67
1	25	3	1.46	5.43	1.39	5.67	16.96	27.65
1	25	4	1.46	5.43	1.39	5.67	39.38	41.33
1	26	1	1.4	6.37	1.34	6.2	60.25	76.85
1	26	2	1.4	6.37	1.34	6.2	82.3	110.81
1	26	3	1.4	6.37	1.34	6.2	59.59	86.38
1	26	4	1.4	6.37	1.34	6.2	42.36	72.25
1	27	1	1.27	4.96	0.9	4	25.18	45.07
1	27	2	1.27	4.96	0.9	4	21.48	40.34
1	27	3	1.27	4.96	0.9	4	24.62	40.82
1	28	1	1.54	6.41	0.97	5.89	57.56	74.94
1	28	2	1.54	6.41	0.97	5.89	98.48	110.36
1	28	3	1.54	6.41	0.97	5.89	94.22	127.71
1	28	4	1.54	6.41	0.97	5.89	51	74.17
1	28	5	1.54	6.41	0.97	5.89	83.37	98.05
1	29	1	1.51	6.21	1.76	7.34	126.91	157.35
1	29	2	1.51	6.21	1.76	7.34	22.58	36.23
1	29	3	1.51	6.21	1.76	7.34	59.26	77.52
1	29	4	1.51	6.21	1.76	7.34	77.14	100.66
1	30	1	1.84	7.47	1.38	7.11	52.11	75.77
1	30	2	1.84	7.47	1.38	7.11	88.38	96.95
1	30	3	1.84	7.47	1.38	7.11	44.2	50.68
1	30	4	1.84	7.47	1.38	7.11	11.42	19.03
2	1	1	2.69	10.27	1.75	7.93	107.3	125.46
2	1	2	2.69	10.27	1.75	7.93	60.96	85.47
2	1	3	2.69	10.27	1.75	7.93	105.34	134.48
2	1	4	2.69	10.27	1.75	7.93	26.34	65.63
2	1	5	2.69	10.27	1.75	7.93	96.24	110.18
2	2	1	2.19	9.00	1.78	7.81	58.66	72.56
2	2	2	2.19	9.00	1.78	7.81	30.76	43.93
2	2	3	2.19	9.00	1.78	7.81	29.31	43.15
2	2	4	2.19	9.00	1.78	7.81	30.58	51.53
2	2	5	2.19	9.00	1.78	7.81	45.93	60.63
2	3	1	2.63	9.45	2.46	9.64	121.8	156.36
2	3	2	2.63	9.45	2.46	9.64	96.34	127.85
2	3	3	2.63	9.45	2.46	9.64	156.5	189.13
2	4	1	2.07	7.88	1.7	7.39	132.93	154.3
2	4	2	2.07	7.88	1.7	7.39	48.46	67.03
2	4	3	2.07	7.88	1.7	7.39	90.09	105.14
2	4	4	2.07	7.88	1.7	7.39	64.11	83.46

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A-1 The analytical results of benzene and toluene concentration in air and in gasoline (Cont.)

Brand	Pump	No. of subject	Benzene in gasoline octane 91(%V)	Toluene in gasoline octane 91 (%V)	Benzene in gasoline octane 95 (%V)	Toluene in gasoline octane 95 (%V)	Benzene concentration in air (ppb)	Toluene concentration in air (ppb)
2	4	5	2.07	7.88	1.7	7.39	89.75	108.56
2	5	1	1.84	8.69	2.27	9.68	116.47	139.72
2	5	2	1.84	8.69	2.27	9.68	129.4	155.1
2	6	1	2.5	8.82	2.07	8.22	40.79	53.27
2	6	2	2.5	8.82	2.07	8.22	23.39	32.44
2	6	3	2.5	8.82	2.07	8.22	19.17	26.34
2	6	4	2.5	8.82	2.07	8.22	134.78	181.71
2	6	5	2.5	8.82	2.07	8.22	16.51	35.79
2	7	1	2.23	8.89	1.76	8.21	52.09	78.8
2	7	2	2.23	8.89	1.76	8.21	66.66	98.06
2	7	3	2.23	8.89	1.76	8.21	27.94	47.03
2	8	1	2.19	7.98	1.92	7.77	44.25	83.81
2	8	2	2.19	7.98	1.92	7.77	76.3	112.17
2	8	3	2.19	7.98	1.92	7.77	48.03	76.77
2	8	4	2.19	7.98	1.92	7.77	21.84	48.55
2	8	5	2.19	7.98	1.92	7.77	64.21	86.29
2	9	1	2.09	8.02	1.36	6.01	4.72	43.51
2	9	2	2.09	8.02	1.36	6.01	14.3	29.46
2	9	3	2.09	8.02	1.36	6.01	18.03	34.19
2	10	1	2.47	9.34	2.33	9	87.27	119.62
2	10	2	2.47	9.34	2.33	9	56.02	83.29
2	10	3	2.47	9.34	2.33	9	96.76	130.76
2	10	4	2.47	9.34	2.33	9	96.63	130.87
2	10	5	2.47	9.34	2.33	9	57.36	73.34
2	11	1	2.49	10.69	2.27	9.85	96.37	129.38
2	11	2	2.49	10.69	2.27	9.85	35	61.93
2	11	3	2.49	10.69	2.27	9.85	59.54	98.6
2	11	4	2.49	10.69	2.27	9.85	81.96	118.5
3	1	1	1.64	10.79	1.62	10.63	71.19	130.07
3	1	2	1.64	10.79	1.62	10.63	93.98	153.02
3	2	1	1.72	18.52	1.33	11.27	50.8	102.65
3	2	2	1.72	18.52	1.33	11.27	35.44	73.02
3	3	1	1.92	12.54	1.3	8.34	66.33	131.67
3	3	2	1.92	12.54	1.3	8.34	46.12	110.3
3	4	1	2.07	12.05	1.43	8.81	35.27	57.09
3	4	2	2.07	12.05	1.43	8.81	70.39	163.27
3	5	1	1.52	10.97	1.51	9.12	57.78	128.71
3	5	2	1.52	10.97	1.51	9.12	47.04	92.97
3	5	3	1.52	10.97	1.51	9.12	64.11	147.05
3	5	4	1.52	10.97	1.51	9.12	87.31	168.72
3	5	5	1.52	10.97	1.51	9.12	42.11	84.78

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APPENDIX B

B-1 The environmental condition and amount of gasoline sold of gasoline station

Brand	Pump	Humidity	Temp. (°C)	Wind speed (m/sec)	Amount of gasoline sold (l)
1	1	65.02	31.28	0.67	4,715
1	2	53.15	34.12	1.01	10,000
1	3	48.75	34.47	0.65	3,667
1	4	51.13	33.84	0.79	9,314
1	5	53.15	34.05	0.67	14,145
1	6	56.77	32.81	1.40	5,930
1	7	54.95	34.43	0.80	5,664
1	8	59.08	32.05	0.81	8,850
1	9	59.4	30.69	0.68	5,093
1	10	76.05	30.94	0.81	4,221
1	11	63.5	32.5	1.08	6,542
1	12	52.36	33.36	1.26	14,406
1	13	68.08	31.64	0.85	7,159
1	14	62.71	32.06	1.39	4,588
1	15	57.42	31.4	0.58	6,490
1	16	49.76	33.43	0.57	16,029
1	17	59.7	31.71	0.59	13,044
1	18	61.93	32.74	0.60	4,856
1	19	53.67	34.39	0.70	4,856
1	20	43.13	34.81	0.90	16,401
1	21	56.56	32.63	0.89	7,507
1	22	41.03	34.01	1.64	2,364
1	23	65.46	31.95	0.60	9,834
1	24	43.73	31.3	1.69	5,550
1	25	52.08	32.27	0.95	2,333
1	26	56.45	33.04	1.04	8,350
1	27	62.65	32.74	1.77	10,390
1	28	61.86	32.56	0.84	12,662
1	29	52.42	33.53	1.00	11,883
1	30	68.75	31.41	1.15	5,526
2	1	56.28	32.38	0.53	19,164
2	2	59.49	33.02	0.77	4,565
2	3	63.69	32.9	0.87	7,706

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B-1 The environmental condition and amount of gasoline sold of gasoline station (Cont.)

Brand	Pump	Humidity	Temp. (°C)	Wind speed (m/sec)	Amount of gasoline sold (l)
2	4	52.23	34.38	0.80	8,997
2	5	54.76	33.21	1.00	10,396
2	6	72.31	31.72	0.97	1,831
2	7	60.15	32.76	0.74	2,419
2	8	55.81	33.65	1.13	2,280
2	9	73.15	31.65	1.05	1,017
2	10	58.43	33.06	0.70	4,642
2	11	59.34	31.09	1.49	2,447
3	1	49.18	30.25	0.62	2,447
3	2	51.67	27.88	1.43	1,742
3	3	51.84	29.08	0.58	2,859
3	4	58.16	26.37	1.05	421
3	5	48.44	29.16	0.88	-

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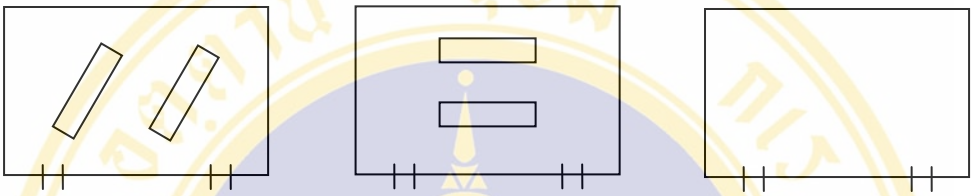
APPENDIX C

แบบฟอร์มการสอบถามข้อมูลเกี่ยวกับสถานีบริการน้ำมันเชื้อเพลิง

ชื่อปั๊ม _____ วันที่ _____

1. รูปแบบ Lay out ของปั๊มน้ำมัน



2. ระยะห่างจากถนนถึงหัวจ่ายที่ใกล้ที่สุด ประมาณ _____ เมตร
3. ปั๊มน้ำมันตั้งอยู่ติดกับถนน _____ เลน
4. จำนวนตู้จ่ายน้ำมัน _____ ตู้/ปั๊ม และจำนวนหัวจ่ายน้ำมัน _____ หัวจ่าย/ตู้
   - เบนซิน ออกเทน 91 _____หัวจ่าย
   - เบนซิน ออกเทน 95 _____หัวจ่าย
   - ดีเซล _____หัวจ่าย
   - _____ หัวจ่าย
5. อัตราการเติมน้ำมันเบนซินของหัวจ่าย _____ ลิตร/นาที
6. มีระบบ Recovery หรือไม่
7. จำนวนเด็กปั๊ม _____ คน
8. ลักษณะการทำงานของเด็กปั๊ม

   ☐ ประจำหัวจ่าย _____ หัวจ่าย ☐ หมุนเวียน _____ หัวจ่าย ☐ อื่นๆ _____
9. ลักษณะการทำงานของเด็กปั๊ม

   ☐ ประจำ ณ หัวจ่าย ขณะเติม ☐ ไม่ประจำ ณ หัวจ่าย ขณะเติม
10. เวลาเฉลี่ยในการเติม _____ นาทีต่อครั้ง
11. ยอดขายน้ำมัน
    - เบนซิน ออกเทน 91 _____ ลิตร
    - เบนซิน ออกเทน 95 _____ ลิตร

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แบบฟอร์มการตรวจวัดปริมาณเบนซินและโทลูอีน ด้วย Chachoal Tube

ชื่อปั๊มน้ำมัน _____ **วันที่ทำการตรวจวัด** _____

NO.	Flow rate	เวลาที่เก็บตัวอย่าง	เพศ/อายุ	ส่วนสูง	การสูบบุหรี่	จำนวนห้วจ่ายที่รับผิดชอบ	ลักษณะงาน	ผลการตรวจวัด
					สูบบุหรี่ (___ มวน) ไม่สูบบุหรี่	เบนซิน 91 _____ ห้วจ่าย เบนซิน 95 _____ ห้วจ่าย ดีเซล _____ ห้วจ่าย		
					สูบบุหรี่ (___ มวน) ไม่สูบบุหรี่	เบนซิน 91 _____ ห้วจ่าย เบนซิน 95 _____ ห้วจ่าย ดีเซล _____ ห้วจ่าย		
					สูบบุหรี่ (___ มวน) ไม่สูบบุหรี่	เบนซิน 91 _____ ห้วจ่าย เบนซิน 95 _____ ห้วจ่าย ดีเซล _____ ห้วจ่าย		
					สูบบุหรี่ (___ มวน) ไม่สูบบุหรี่	เบนซิน 91 _____ ห้วจ่าย เบนซิน 95 _____ ห้วจ่าย ดีเซล _____ ห้วจ่าย		
					สูบบุหรี่ (___ มวน) ไม่สูบบุหรี่	เบนซิน 91 _____ ห้วจ่าย เบนซิน 95 _____ ห้วจ่าย ดีเซล _____ ห้วจ่าย		

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BIOGRAPHY

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