

CHAPTER 1

INTRODUCTION

1.1 Air pollution

Air pollution is one of the most important environmental issues which is still to be solved (Mage *et al.*, 1996; Fenger, 1999; Faiz and Sturm, 2000), and has far-reaching impacts on the sustainable development of the terrestrial biosphere and exposure to polluted air causes adverse human health effects. Previous studies have linked elevated levels of air pollutants to many human health problems such as low birth weight and birth defects, infant mortality, child asthma, increased hospital admittance, increased allergy cases, lung disease, respiratory and cardiovascular disease and mortality displacement (Bates, 1992, Ostro *et al.*, 1996, Brunekreef, 1999, Kunzli *et al.*, 2000). Therefore, characterizing air pollution distribution and understanding its causes and variations in megacities has become an urgent issue for policy makers (Wang *et al.*, 2004).

Important effort has been invested around the world to study regional air pollution problems and their control. Maximum the problem list are urban air pollution and road traffic (Faiz and Sturm, 2000; Sturm, 2000). Air pollutant concentrations in megacities are dominated by the exhaust emissions of CO, SO₂, NO_x, NMHCs (non-methane hydrocarbons) and suspended from vehicle usage (Fenger, 1999). This leads to concerns about the projected pollution levels and effects on human health in increasingly cities which are congested from car.

Air quality has become a big problem and has been steadily deteriorating over the past ten years of Chiang Mai (Chunram *et al.*, 2007). The fact that, the

geographical features of Chiang Mai City's located in a natural bowl that results in the same air being re-circulated, picking up more pollutants every time. Anthropogenic activities including cremation, garbage burning, forest fire and vehicle emission are the main contribution of air pollutants in Chiang Mai City.

1.2 Nitrogen dioxide (NO₂)

Nitrogen dioxide (NO₂) is an important indicator of air pollution, because the concentration of NO₂ is well correlated with the concentration of carbon monoxide (CO), particulate polycyclic aromatic hydrocarbons (PAHs) (Lewis *et al.*, 1995) and soot (Bower *et al.*, 1991). It is the most toxic form of nitrogen oxides (NO_x) (Glasius *et al.*, 1999) generated from motor vehicles or traffic, which is a major source of ambient air, electric utilities, fossil fuel combustion, primary metal production and incineration. Natural sources of NO_x include lightning and the aerobic activity of soil bacteria. These natural sources, however, are small compared to emissions caused by human activity. Sources of NO₂ are shown in Figure 1.1.

1.2.1 Health and environmental effects of NO₂

Inhalation of nitrogen dioxide has a strong respiratory irritant. Like other gases with low to moderate solubility in water (e.g., ozone), nitrogen dioxide reaches deeper regions of the respiratory tract. The bronchotracheal and alveolar region are the predominating sites of action (Kraft *et al.*, 2005). Nitrogen dioxide has reduce resistance against respiratory infections (Chauhan *et al.*, 1998), lung function changes in asthmatics (Avol *et al.*, 1989) and enhance bronchial responsiveness to allergens (Tunnicliffe *et al.*, 1994).

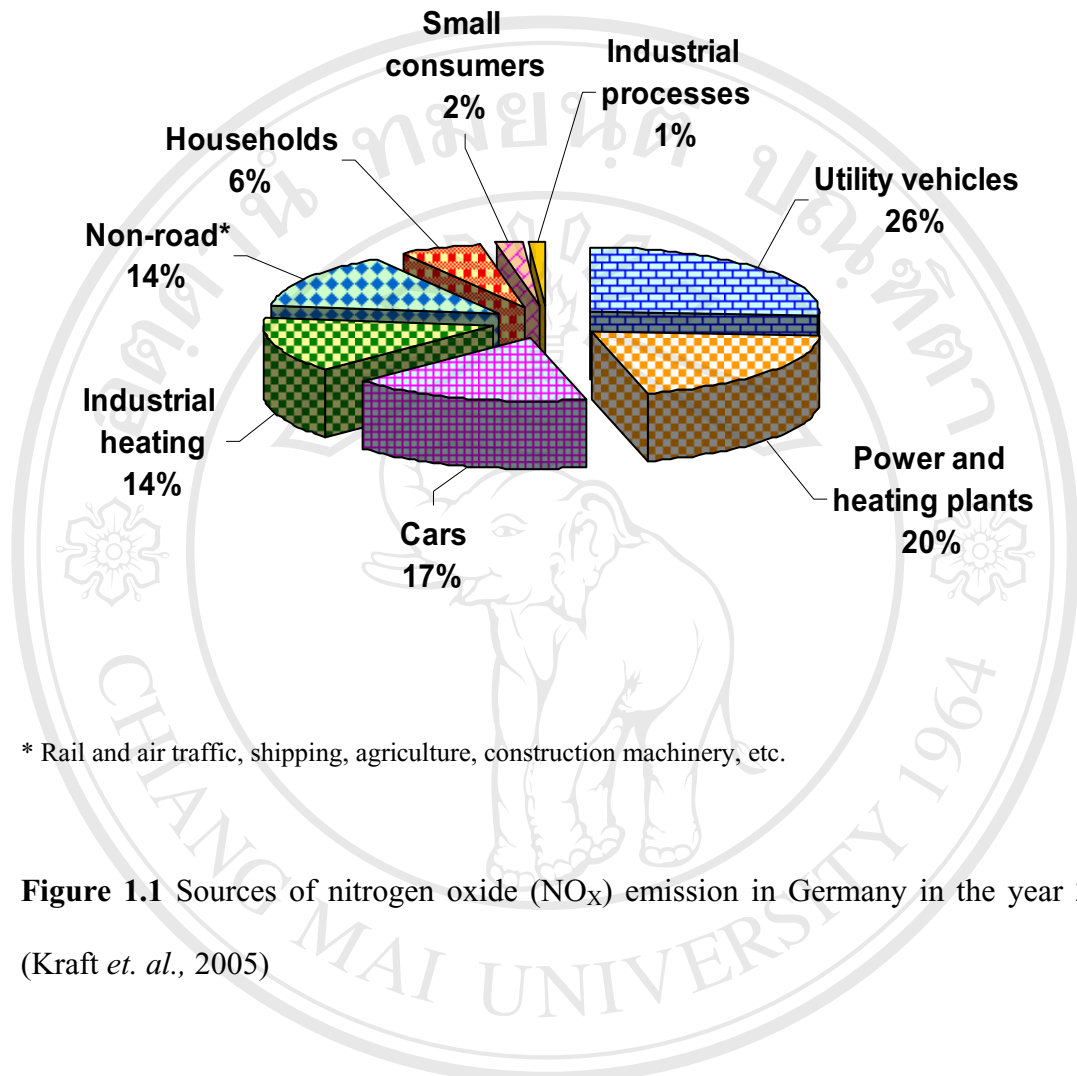


Figure 1.1 Sources of nitrogen oxide (NO_x) emission in Germany in the year 2000 (Kraft *et. al.*, 2005)

Nitrogen dioxide chemically transforms into nitric acid, when deposited contributes to lake acidification. Nitrogen dioxide, when chemically transformed to nitric acid, can corrode metals, fade fabrics and degrade rubber. It can damage trees and crops, resulting in substantial losses (Cox, 2003 and Verma *et al.*, 2008). However, Air quality standard of Thailand was created by PCD. For 1 hour, NO₂ concentrations should not exceed 320 µg/m³ or 170 ppbv. This standard level is higher than other counties including such as EU and New Zealand as shown in Table 1.1.

Table 1.1 Standard of nitrogen dioxide in ambient air prescribed by various organizations

Organization	Average	NO ₂ standard level		
		ppm	µg/m ³	ppbv*
EU ^a	1 hour	0.106	200	106
	Annual	0.021	40	21
U.S.-EPA ^b	Annual	0.053	100	53
WHO ^c (guideline)	1 hour	0.106	200	106
	Annual	0.021	40	21
Ministry for the Environment,	1 hour	0.106	200	106
New Zealand ^d	24 hours	0.053	100	53
PCD, Thailand ^e	1 hour	0.17	320	170

* an ambient pressure of 1 atm and temperature 25 °C

Remarks and sources:

a; Eupean union (<http://ec.europa.eu/environment/air/quality.htm>)

b; United State Environmental Protection Agency (<http://www.epa.gov/air/criteria.html>)

c; World Health Organization (WHO, 2005)

d; <http://www.mfe.govt.nz/publications/air/air-quality-tech-report43/html/page6.html>)

e; Pollution Control Department, Thailand (http://www.pcd.go.th/info_serv

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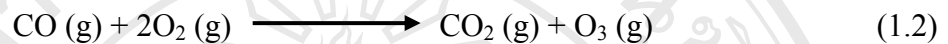
1.2.2 Atmospheric reaction of nitrogen

Atmospheric reaction of nitrogen is much more complex than the atmospheric reaction of sulfur. Ammonia (NH_3) is the most reduced form of nitrogen, and is released in small quantities from anaerobic degradation of organic matter containing nitrogen. Just like hydrogen sulfide (H_2S), ammonia reacts with the hydroxyl radical to form oxidized nitrogen species. Nitrogen oxides are released to the atmosphere from both natural and anthropogenic sources. The two most common nitrogen gases released to the atmosphere from biological processes are nitrous oxide (N_2O) and nitrogen dioxide (NO_2). Combustion processes release mostly nitrogen oxide (NO) and nitrogen dioxide. The exact composition of nitrogen oxides emitted from combustion processes varies with temperature of the combustion process, and the nitrogen oxides from combustion are often referred to as NO_x to indicate the uncertainty in chemical composition. Like sulfur, the modern global nitrogen cycle is very different than the “pre-industrial” nitrogen cycle. The difference, again, is the large amount of nitrogen added to the atmosphere through combustion processes. The excess atmospheric nitrogen oxides contribute to acid rain in the same way that excess sulfur oxides do (Environment Canada, 2004).

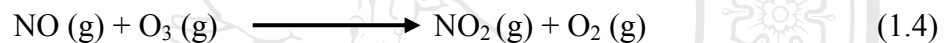
Colls (2002) notes that the nitrogen dioxide (NO_2) found in the atmosphere was released in nitric oxide (NO) form from sources. The remainder has been created in the atmosphere as part of the same photochemical activity that is responsible for ozone (O_3) formation, which ozone is formed in the troposphere from incomplete combustion processes of nitrogen dioxide and carbon monoxide and from the photolysis of molecular oxygen (O_2) in the stratosphere as shown in the reaction (1.1), (1.2) and (1.3), respectively. The nitric oxide from fossil fuel combustion reacts with ozone as

shown in the reaction (1.4). Some of the nitric oxide (NO) reacts with oxygen to form nitrogen dioxide as shown in reaction (1.5).

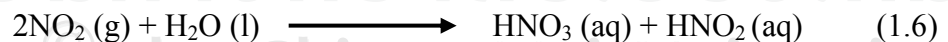
In the troposphere;



In the stratosphere;



During day light, the NO_2 absorbs blue and ultraviolet (UV) radiation lower than 420 nm and decomposes back to NO and O_3 , resulting in a photochemical equilibrium between the four gases. In rural areas, away from the NO sources, the NO_2 concentration is usually considerably higher than that of NO. In urban areas, the O_3 becomes depleted and the balance moves in favour of NO. Nitrogen dioxides (NO_2) in the atmosphere reacts with water to form nitric or nitrous acid follow the reaction (1.6). The principal sink for NO_x is oxidation to nitric acid (HNO_3).



In day time, reaction 1.7 become much less important at night because the hydroxyl radical is primary formed photochemically. At night, ozone will reacts with NO_2 to form nitrate (NO_3), which rapidly reacts with NO_2 to form dinitrogen pentoxide (N_2O_5). The N_2O_5 will react with water in droplets in the atmosphere and convert to nitric acid (reaction 1.8 to 1.10).



When the nitrogen dioxide (NO_2) concentration is well above clean air levels and there is plenty of sunlight, then an oxygen atom splits off from the nitrogen dioxide molecule as in reaction (1.11). Oxygen radical (O^\bullet) is then reacted with O_2 in air and produces O_3 (1.12)



Varshney and Singh (2003) notes peroxyacetyl nitrate (PAN) is produced in the troposphere by photochemical oxidation of carbonyl compounds in the presence of NO_2 as shown in the reaction (1.13).



Colls (2002) reported PAN is only slightly soluble in water, it is not removed effectively by precipitation processes. The main loss route is by thermal decomposition which regenerates NO_2 as shown in me (1.14).



Note; M is any third body molecule, which is required for energy absorption but which does not take part in the reaction as such.

1.3 Study site “Chiang Mai Province”

1.3.1 Geographical background, population and economic structure

Chiang Mai is Thailand's northern capital. It is the country's second largest city, but while Bangkok. It is located about 310 meters above sea level and at latitude 17° 15' to 20° 10' N and longitude 98° 5' to 99° 35' E (Department of Curriculum and Instruction Development, 2000). Its total land area is 20,107.057 km² or 12,566,910 Rai. It is located about 700 kilometers north of Bangkok, among some of the highest mountains in the country (Vatanasapt, 1993). The city stands on the Ping river, a major tributary of the Chao Phraya river. Chiang Mai's topography can be divided into two groups, which are mountainous areas, Mountainous areas and valley, and plains. Mountainous areas with an elevation greater than 500 meters make up about 80 percent of Chiang Mai's land and are most often covered with forests, making them unsuitable for agricultural purposes. Most of these mountains are located to the north and south of the province. Valley and plains run in a north-south pattern. They are found mostly nearby the river's bank and between mountain ranges. Being both flat and fertile, these areas are extremely suitable for agriculture. Forests areas are approximately 15,667.42 km² (77.92 %). Agricultural land is approximately 3,659.48 km² (18.20 %). Communities are about 597.18 km² (2.97 %). Water source is approximately 172.92 km² (0.86 %). Industrial is approximately 8.04 km² (0.04 %). Location of Chiang Mai Province is shown in Figure 1.2 (Chiang Mai Provincial Operation Center, 2008).

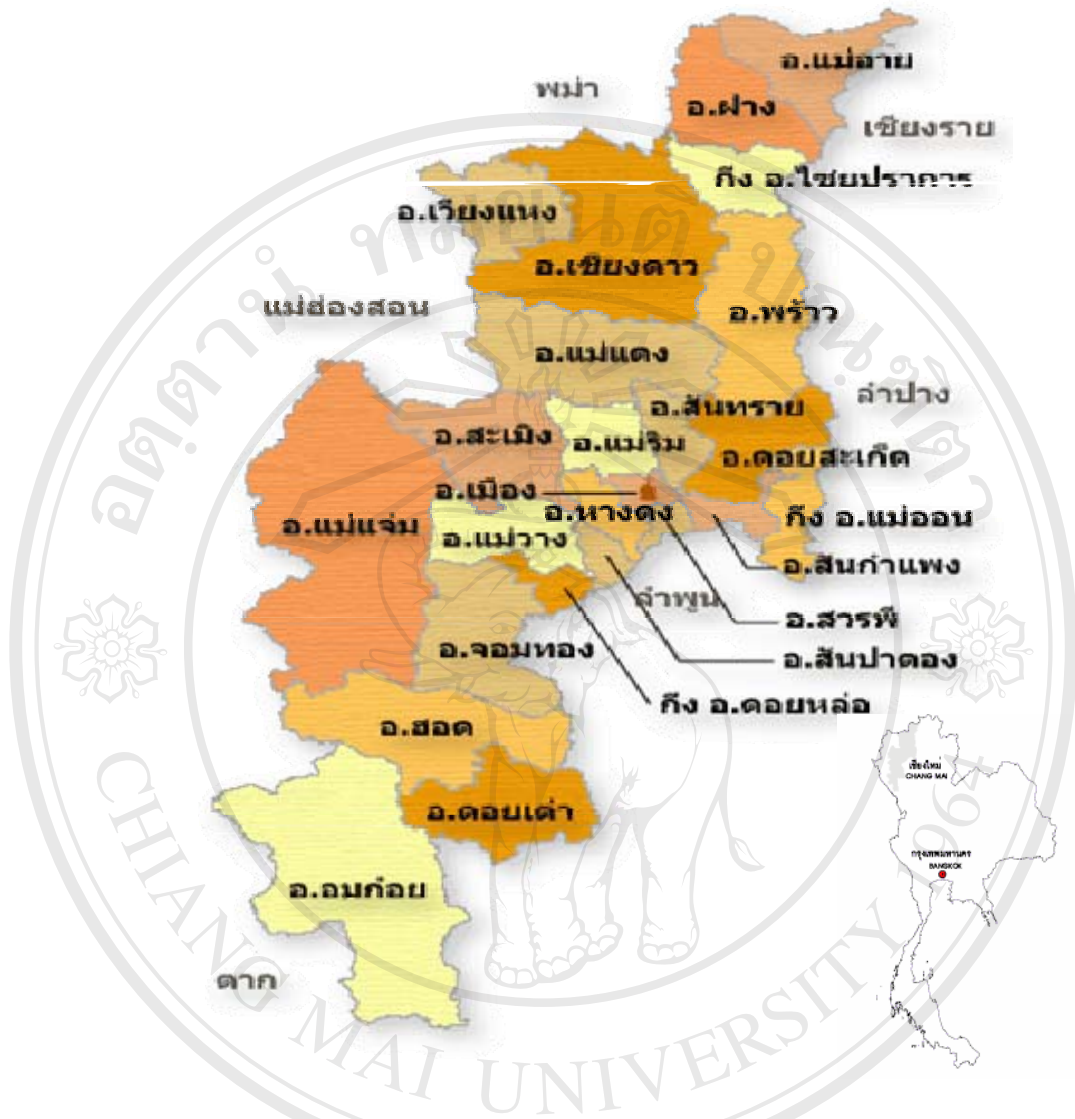


Figure 1.2 Map of Thailand, including location of Chiang Mai

(<http://www.chiangmai.go.th>)

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่

The Chiang Mai Province is subdivided into 24 districts (Amphoe). The districts are further subdivided into 204 sub-districts (Tambon) and 1,915 villages (Muban). Chiang Mai Province has a total population of 1,673,813 with 822,358 males and 851,455 females (statistic from October 2007). There are approximately 829,400 families and the population density averages 83.24 people per km² in the province

(Chiang Mai Provincial Operation Center, 2008). The population density of districts in Chiang Mai Province in 2006 is shown in Table 1.2

In relation to the rest of Thailand, Chiang Mai's year round weather is considered to be relatively cool. The annual average temperature is 25.6 °C. The highest temperature is 31.9 °C and the lowest is 20.7 °C. The annual average humidity is 75 %. An annual average number of rainy days are around 99, while the total rainfall is around 1,125.3 mm (Northern Meteorological Center, 2007).

The Southwest, Northwest and Southeast monsoons are the three main factors influencing season of Chiang Mai to be three seasons as in the following. The rainy season, influenced by the southwest monsoon, begins in mid-May and continues until October. The cold season begins in November and continues until March and is influenced by the Northwest monsoon, which brings cold air from Siberia, through China and down into Northern Thailand. The hot season begins in March to mid-May and is influenced by the Southeast monsoon.

The most important occupations are cultivation of rice, peanuts, soy beans, longan, lychee, strawberries and tobacco, weaving, wood products and handicrafts. Other local activities include the tobacco leaf drying industry, rice milling, foods and beverage industries. In recent years, Chiang Mai has become an increasingly modern city, although it lacks the cosmopolitan gloss of Bangkok. It has many attractions for the thousands of foreign visitors who come each year. Chiang Mai's historic importance is derived from its important strategic location on an ancient trade route. Long before the modern influx of foreign visitors, the city served as an important centre for handcrafted goods, umbrellas, jewelry (particularly silver) and woodcarving.

Table 1.2 Population and population density in Chiang Mai Province

Districts (Amphoe)	Thai name	Area (km ²)	Population (people)	Population density (people/km ²)
Muang Chiang Mai	เมืองเชียงใหม่	166.47	243,065	1,460.10
Chom Thong	จอมทอง	711.30	65,563	92.17
Mae Chaem	แม่แจ่ม	3,361.15	67,055	19.95
Chiang Dao	เชียงดาว	2,052.00	87,071	42.43
Doi Saket	ดอยสะเก็ด	749.00	64,847	86.58
Mae Taeng	แม่แตง	1,362.78	75,784	55.61
Mae Rim	แม่ริม	495.00	83,716	169.12
Samoeng	สะเมิง	1,002.00	23,301	23.25
Fang	ฝาง	888.16	121,374	136.66
Mae Ai	แม่สาย	736.70	77,490	105.19
Phrao	พร้าว	2,021.86	51,844	25.64
San Pa Tong	สันป่าตอง	178.18	76,612	429.97
San Kamphaeng	สันกำแพง	197.83	74,488	376.52
Sansai	สันทราย	285.02	108,352	380.16
Hang Dong	หางดง	302.00	73,538	243.50
Hot	ฮอด	1,430.38	43,843	30.65
Doi Tao	ดอยเต่า	803.90	27,186	33.82
Omroi	อมก๋อย	2,336.27	60,737	26.00
Saraphi	สารภี	97.45	75,196	771.64
Wiang Haeng	เวียงแหง	705.00	29,279	41.53
Chai Prakan	ไชยปราการ	521.30	47,926	91.94
Mae Wang	แม่วาง	601.68	30,859	51.29
Mae On	แม่ออน	492.83	21,726	44.08
Doi Lo	ดอยหล่อ	219.00	27,446	125.32

Source: Chiang Mai Provincial Operation Center, Chiang Mai (2006)

1.3.2 Traffic structure

Data of the registration of all types of vehicles in Chiang Mai Province presented that the number of vehicles increased from 21,335 in 1999 to 64,462 in 2007. In 2007, number of motorcycles registered were approximately 48,256 (74.9%) number increased from 16,623 vehicles in 1999. From the number of 64,462 vehicles in 2007, it includes 48,256 (74.9%) motorcycles, 8,077 (12.5%) personal car, 6,864 (10.6%) pick-up cars and 2% of others i.e. buses, tractors, etc. Figure 1.3 presents the population from 2001 to 2006 of Chiang Mai Province in parallel with the number of the registration of vehicles (Chiang Mai Land Transport Bureau, Department of Land Transport, Ministry of Transport, 2008). Gasoline was used in personal car and motorcycle, while diesel was used in bus, train, truck and pick-up (Office of Energy Regional 9, Phitsanulok, 2004).

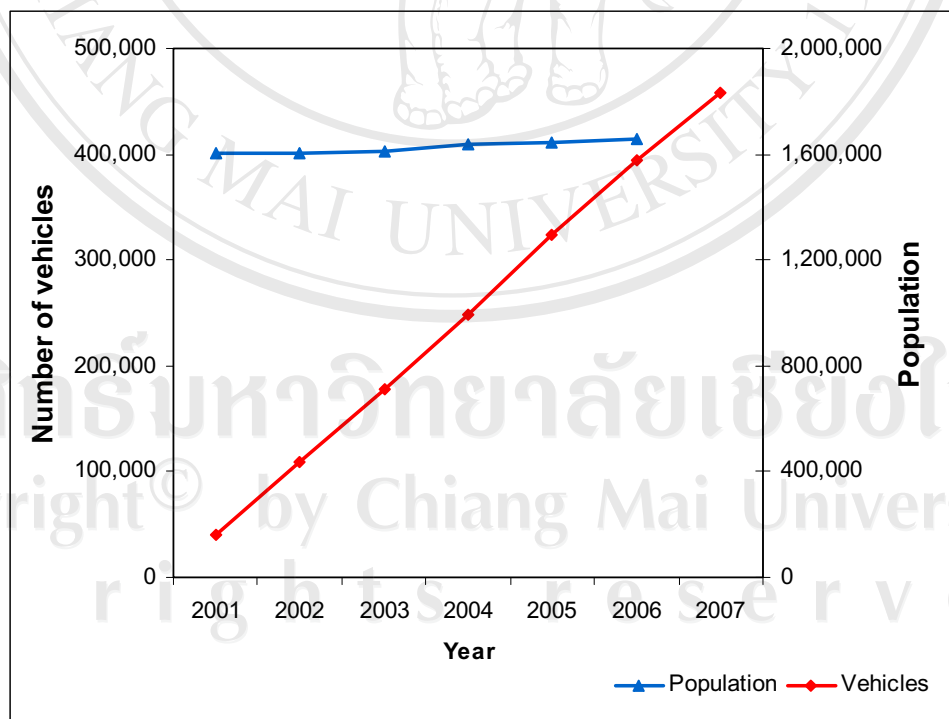


Figure 1.3 Changes in the population and the number of the registered vehicles in Chiang Mai Province from 2001 to 2006

1.4 Passive sampling of air

The passive sampling is defined as any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media (Gorecki and Namiesnik, 2002). It can be used for the determination of both inorganic and organic compounds in a variety of matrices, including air, water and soil.

In recent years, passive samplers have been gaining increasing attention because they are simple, lightweight and cheap devices, which operate without any power source. Passive samplers have been found to be efficient, cost effective and free from the need for elaborate calibration and maintenance. It can be fixed to any objects and on persons, depending on the objective of the measurement. Passive sampler remain stable over several months after sampling and can be conveniently transported before and after exposure. Also all sampler parts are reusable. Hence, they are ideally suited for developing a wide spatial network for nitrogen dioxide monitoring. In addition, specific passive samplers have been also developed for measuring water vapour, sulphur dioxide, benzene, aniline, ammonia, carbon monoxide, ozone, nitric oxide and some volatile organics. In some countries, Central America, UK, Switzerland, France, Italy, Brazil, Turkey, Argentina, and China, passive samplers have been used for monitoring NO₂ levels in an ambient environment. In the UK, an elaborate NO₂ monitoring network, involving more than 1,200 monitoring sites and 330 local authorities is in operation using passive samplers. It is ideally suited for wide spatial measurement of NO₂ (Varshney and Singh, 2003).

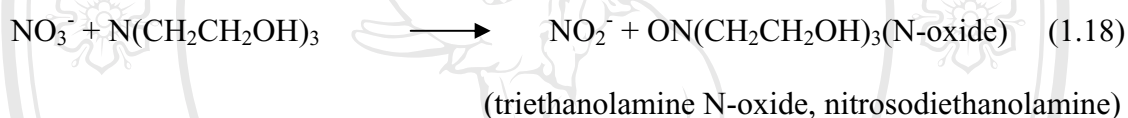
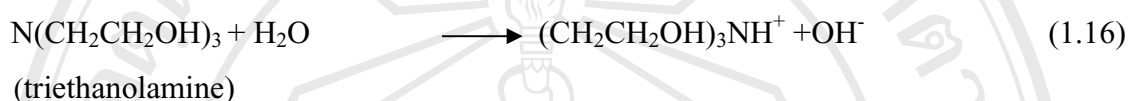
1.4.1 Operating principle

A passive sampler is a device which is capable of taking samples of gases or vapors to collection medium from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but does not involve the active movement of air through the device (Brown, 2000). The driving force is the concentration gradient between the surrounding air and the absorbing surface, where the pollutant concentration is zero. The passive sampler is based on the principle of diffusion of air. The ambient air NO_2 diffuses up the passive sampler where it gets absorbed on the triethanolamine (TEA) impregnated mesh. Ozden and Dogeroglu (2007) and Chalermrom (2008) used 20 % TEA impregnated Whatman GF/A fiber glass filter paper in passive sampler, which NO_2 is absorbed in ambient air and contented of nitrite ions. The product of absorption of NO_2 in TEA solution is nitrosodiethanolamine (Aoyama and Yoshiro, 1983 cited by Glasius *et al.*, 1999). The compound can be determined by spectrophotometry. Glasius *et al.* (1999) identified it as triethanolamine N-oxide and the following reaction scheme was proposed. TEA is absorbed SO_2 in ambient air, which it's absorbed in form of sulfate ions (Krochmal and Kalina, 1997) and SO_2 can interference of NO_2 absorption. SO_2 of in ambient air fewer concentrations than NO_2 , therefore SO_2 are no interfere to measurement NO_2 in this work. Although Hisham and Grosjean (1990) noted that PAN (peroxyacetyl nitrate) was a severe interferent to quantification of NO_2 by TEA diffusion tube. However, Gair *et al.* (1991) reported not interference is caused by the presence of PAN, which can provide NO_2^- in complex with TEA. The concentrations of PAN are unlikely to be sustained for long periods during diffusion sampler exposure and it's

likely to be negligible (Heal and Cape, 1997). The actual effect of PAN may be even less in actual practice because of the thermal equilibrium existing between PAN and NO_2 (Varshney and Singh, 2003). Glasius *et al.* (1999) proposed the reaction product as triethanolamine N – oxide on the basis of the following reaction.



This mechanism was obtained from the reaction as shown below.



Nitrite (NO_2^-) can be determined by spectrophotometry. Nitrite in solution reacts with sulphanilamide and form a diazonium compound, which on coupling with NEDA form purple azodye (Varshney and Singh, 2003). The reactions involved are shown in Figure 1.5.

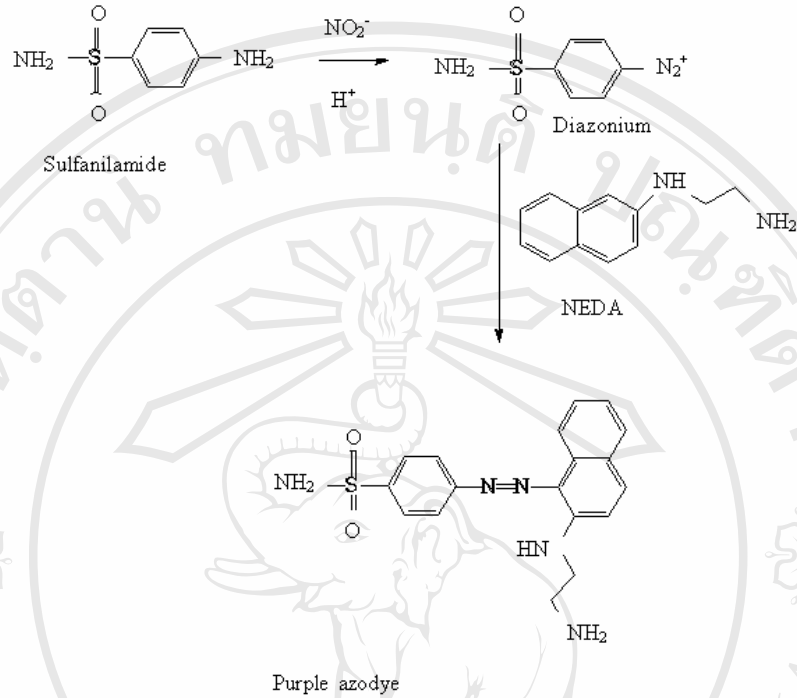


Figure 1.4 The NO_2^- formation for determination by spectrophotometry

The principle of diffusion in passive sampling refer to Fick's First Law as describe by Gair *et al.* (1991). The unidirectional flow of gas_1 through gas_2 is given as the following.

$$F_1 = -D_{1,2} \frac{dc_1}{dz} \quad (1.19)$$

Where:

F_1 the flux of gas ($\text{mol cm}^{-2} \text{s}^{-1}$)

$D_{1,2}$ the diffusion coefficient of gas_1 in gas_2 ($\text{cm}^2 \text{s}^{-1}$)

c_1 the concentration of gas_1 in gas_2 (mol cm^{-3})

z the length of diffusion (cm)

The quantity of gas transferred (Q_1 mol) in t seconds for a cylinder of radius r is given by the following equations;

$$Q_1 = F_1 (\pi r^2) t \text{ mol} \quad (1.20)$$

Therefore

$$Q_1 = -D_{12} (c_1 - c_0) (\pi r^2) t / z \text{ mol} \quad (1.21)$$

Where:

c_0 is the concentration experienced at the absorber surface, therefore $(c_1 - c_0)/z$ is the concentration gradient along the cylinder length (z). If an efficient absorber is used to remove gas, then c_0 efficiently becomes zero.

Then the concentration of NO_2 in $\mu\text{g m}^{-3}$ are calculated by applying the equation (Ozden and Dogeroglu, 2007);

$$C = \frac{Q \times z}{\pi r^2 \times t \times D} \quad (1.22)$$

Where

C the concentration measured by passive sampling tube ($\mu\text{g m}^{-3}$)

Q the quantity of absorption products present in the sampler (μg)

r the radius of diffusion tube (m)

t the sampling time (s)

z the diffusion length (m)

D the diffusion coefficient (m^2s^{-1}), $0.154 \times 10^{-4} \text{ m}^2\text{s}^{-1}$ for NO_2

The calculation of gas quantity presented in diffusion tube is depended on the final product after reacting with sampling medium. The detail is shown in appendix A.

1.5 Literature Review

The passive sampler was first developed in U.S.A as an air sampler on worker by Palmes *et al.* (1976), for use in occupational hygiene studies. Since then the passive sampler for NO₂ has been widely used for monitoring air quality for example inside homes, in rural areas and in epidemiological surveys (Glasius *et al.*, 1999). Later, a variety of passive samplers such as tube type, badge type and high efficiency passive samplers were developed (Palmes *et al.*, 1976; Mulik *et al.*, 1989; Krochmal and Gorski, 1991). Out of these, two types namely the tube type (Palmes *et al.*, 1976) and badge type sampler (Krochmal and Gorski, 1991) have been used. However, both tube and badge types of samplers with slight modification serve satisfactory. Different studies have shown that both samplers are suitable for determining real variations in NO₂ concentrations in urban or rural areas (Varshney and Singh, 2003). Some typical physical sampler configurations are shown in Figure 1.5.

Gilbert *et al.* (2003) used Ogawa passive samplers (using triethanolamine-impregnated filters as an absorbent) monitoring nitrogen dioxide (NO₂) from a major highway in Montreal, Canada. They were installed for 7 days in groups of two or three along an axis perpendicular to a major highway where traffic density exceeds 100,000 vehicles / day. Distances ranged from 0 to 1,310 m from the highway. Concentration of NO₂ ranged from 11.9 to 29.3 ppb. Panyaping (2003) used Ogawa sampler and simple passive sampler made from re-used material (film box) monitoring nitrogen dioxide (NO₂) from traffic in urban area locations of Chiang Mai City. Passive

samplings were exposed 24 hr for 3 times per week in both week and weekend days (Friday-Saturday, Saturday-Sunday and Monday-Tuesday) during 1996-2000. Concentration of NO_2 in the winter season was higher than that in rainy season due to several factors such as the lower air ventilation and higher traveling in the high season.

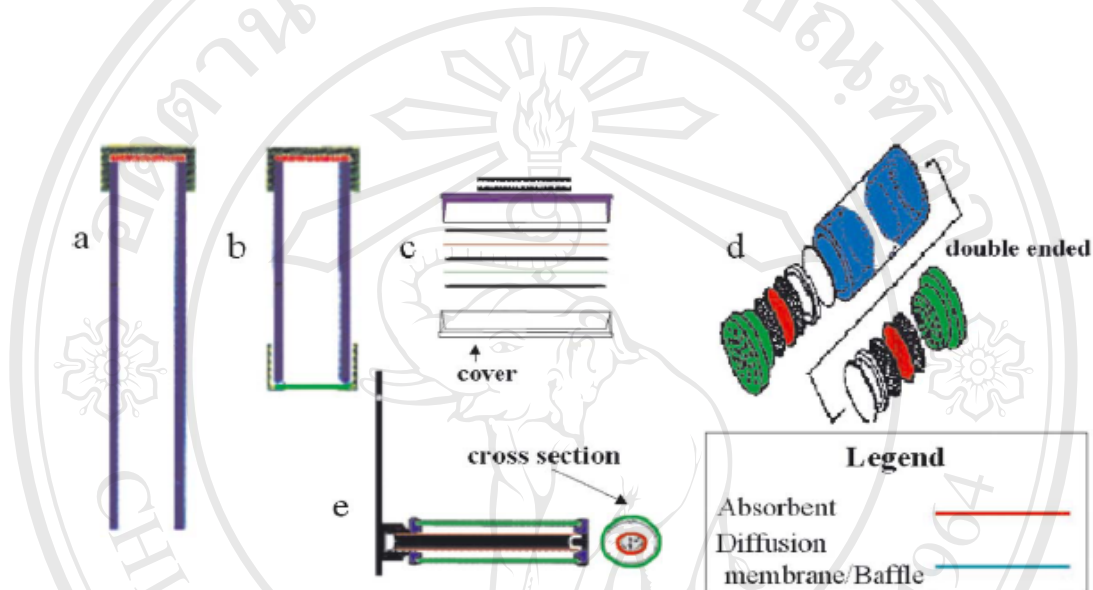


Figure 1.5 Examples of different sampler configurations: (a) open-ended diffusion tube, (b) shorter diffusion tube with diffusion membrane at opening, (c) badge-type with diffusion membrane at opening, (d) double-ended badge with baffles at opening, (e) cylindrical badge with tubular diffusion membrane (Cox, 2003).

Atkin and Lee (1995) used passive diffusion tube sampler monitoring nitrogen dioxide (NO_2) in rural locations of United Kingdom between June 1987 and May 1990 and described for the annual period June 1987-May 1988 and the summer and winter seasons from 57 sites. They found that the winter high value NO_2 concentration were attributed to some seasonality in emissions, and meteorological condition allowing concentrations to build up coupled with a lower rate of daytime conversion by reaction

with OH[•]. The summer low value NO₂ concentration were thought to be principally the result of the greater atmospheric mixing, a higher rate of atmospheric conversion by reaction with OH[•] during the daytime and to a lesser extent, enhanced dry deposition by stomatal uptake.

Stevenson *et al.* (2001) used diffusion tube samplers monitoring nitrogen dioxide (NO₂) of urban areas in UK between 1993 to 1997 inclusive and has shown that highest concentrations occurred in London and urban areas of Yorkshire and Humberside and the East and West Midlands of the UK. Averaged over the whole of the UK, NO₂ concentrations have been remarkably similar for most of the 5 years, though a significant decrease was observed at urban background locations in 1997. Overall, average NO₂ concentrations during 1997 were 23 ppb at kerbside locations and 13 ppb at urban background locations. Fagundez *et al.* (2001) employed passive diffusion sampler monitoring a preliminary air pollution such as nitrogen dioxide (NO₂), total suspended particulate matter (TSPM) and sulphur dioxide (SO₂) in downtown compared with an urban background site in San Miguel (Buenos Aires Metropolitan Area). They found that, the levels for the investigated pollutants are below EPA's guideline values.

Heal and Cape (1997) measured NO₂ concentrations in urban and rural ambient air by using passive diffusion samplers with TEA as adsorbent. The interferences from peroxyacetyl nitrate (PAN) and other were observed to be low for British conditions. The systematic error of within-tube chemistry was also known to be responsible for overestimation of NO₂ by the diffusion sampler, which previously was thought to be due to wind effects. They found that passive sampling is more efficient in rural ambient air compared to urban ambient air. The combined error due to the effect of

wind on path length and chemical effect with cities caused up to 70% overestimation of NO₂. The scientists in Lithuanian capital Vilnius used passive diffusion samplers for evaluation of NO₂ concentration. The NO₂ average rates depend strongly on traffic (sampling place) and are highest concentration range of 52-82 µg/m³ in crossroads and lowest concentration range of 9-16 µg/m³ at the background-suburban level (Perkauskas and Mikeliniskiene, 1998). Ferm and Svanberg (1998) used diffusive (passive) sampler measurements of SO₂ and NO₂ from urban area in Sweden. They were measured on monthly comparison between diffusive and active sampling. Concentration of NO₂ ranged from 0.1-200 µg/m³ for SO₂ and 0.1-400 µg/m³ for NO₂.

Influence of meteorological factors like temperature, relative humidity and wind velocity on the sampling rate of nitrogen dioxide the greatest effect is observed for the wind velocity with significant increase of sampling rate (Plasance *et al.*, 2004). To overcome the problem of wind sensitivity and of low resolution retention time, passive samplers characterized by a large ratio of cross-sectional area to length of diffusion path have been developed (De Santis *et al.*, 2001).

Cox (2003) reported that the most commonly used absorbent sink for NO₂ is triethanolamine (TEA) where the gas is converted to nitrite ion. This has been used in open diffusion tubes or in membrane covered badges (Mulik *et al.*, 1989). A lack of specificity of TEA towards of NO₂ can cause problems as sulfur dioxide (SO₂) is also absorbed, acidifying the TEA reagent and reducing collection efficiency. Limiting exposure of the sampler to one or two weeks can reduce this interference by SO₂ (Heal and Cape, 1997; Ferm and Svanberg, 1998), and suspected loss of NO₂ due to photo degradation of TEA in bright condition (Tang *et al.*, 2001). The diffusion tube samplers and blank must be stored in a fridge at 0°C prior to analysis (Krochmal and

Kalina, 1997). Ozden and Dogeroglu (2007) reported the samplers could be stored for 6 week safely. However, the sampler results were stored at room temperature and in refrigerator no significant difference (Krochmal and Kalina, 1997; Ozden and Dogeroglu, 2007).

Techniques which have been used for determination of NO_2 in the samples are ion chromatography and spectrophotometry. Gilbert *et al.* (2003) analyzed nitrite (NO_2^-) content in samples by ion chromatography (DionexTM 4 X 250 mm AS4A column at a 2 ml/min flow rate, UV absorbance detection wavelength of 220 nm and absorbance output of 0.1 AU). Glasius *et al.* (1999) analyzed concentrations of nitrate in the extract by ion chromatography on a Shimadzu LC – 10A HPLC system with a Shim-Pack IC-A1S column (polymethacrylate support with a quarternary ammonium base as the functional group). The mobile phase was 2.5 mM phthalic acid and 2.4 mM tris(hydroxymethyl)aminomethane (pH 4).

Delgado-Saborit and Esteve-Cano (2006) determined NO_2 colorimetrically as nitrite (NO_2^-) by spectrophotometer at 540 nm. Ogawa passive samplers were used to measure concentrations of NO_x and NO_2 in Oslo, Norway. The developed color was measured by 540 nm on a spectrophotometer (Madsen *et al.*, 2007).

1.6 NO_2 Test Kit

Test kits are self- contained analytical kits that use a chemical reaction that produces color to identify contaminants, both qualitatively and quantitatively. There are numerous advantages to use test kits in the environmental field, including simple equipment, ease of use, quickly to analysis and low cost per sample. The change in color indicates the presence of the target compound, while the compounds are

quantified if the intensity of the color produced can be compared with the color of standard of known concentrations. The level of certainty will vary depending on whether the intensity of the color is compared visually with the standard color chart (<http://www.clu-in.org/char/technologies/color.cfm>).

The NO₂ test kit used in this work was fabricated by Chalermrom (2008), Environmental Chemistry Research Laboratory (ECRL), Chemistry Department, Chiang Mai University. It measures the difference of color intensity by comparison to a standard color chart. The test kit composes of polypropylene (PP) diffusion tube, standard color chart, a plastic shelter, chemical reagents, small glass tube, a plastic dropper and a disposable syringe as shown Figure 1.6.



Figure 1.6 the NO₂ test kit (Chalermrom, 2008)

1.7 Spectrophotometry

The spectrophotometer measures quantitatively the fraction of light that passes through a given solution. In a spectrophotometer, a light from the lamp is guided through a monochromator, which picks light of one particular wavelength out of the continuous spectrum. This light passes through the sample that is being measured. After the sample, the intensity of the remaining light is measured with a photodiode or other light sensor and the transmittance for this wavelength is then calculated. Samples are usually prepared in cuvettes; depending on the region of interest, they may be constructed of glass, plastic or quartz. The diagram of spectrophotometric system is shown in Figure 1.7.

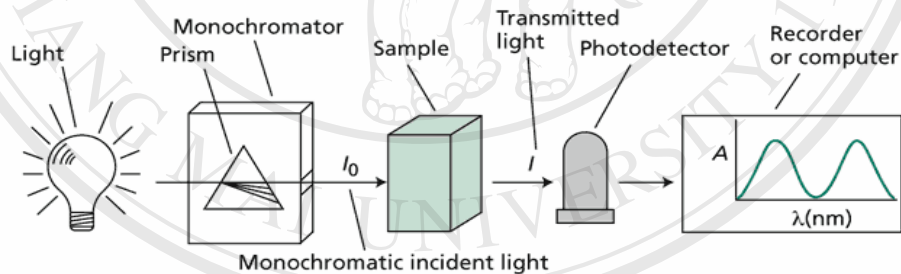


Figure 1.7 Schematic diagram of a spectrophotometer

(<http://4e.plantphys.net/article.php?ch=7&id=66>)

The absorbance of a sample can be related to the concentration of the absorbing species through **Beer's law**:

$$\text{Log } (I_0/I) = A = \epsilon cl \quad (1.23)$$

where A is absorbance, c is concentration, usually measured in moles per liter; l is the length of the light path, usually 1 cm; ϵ is molar absorptivity; I_0 is the intensity of light entering the sample and I is the intensity of light leaving the sample.

The reason that spectrophotometry was used for determination of NO_2 concentration in this research is that the NO_2 test kit was developed from spectrophotometry technique, which is a technique that measures color intensity of nitrite solution from the extracted sample. Therefore, the spectrophotometry was selected for comparison with the NO_2 test kit fabricated by Chalermrom (2008). Spectrophotometry was popular for measurement of NO_2 concentrations in ambient air by passive sampler. [Heal and Cape \(1999\)](#) determined NO_2 colorimetric as nitrite solution by absorption at 540 nm of spectrophotometer. The NO_2 in ambient air was determined by spectrophotometer at a wavelength of 545 nm ([Panyaping, 2003](#)), etc.

1.8 Research Objectives

To monitor and compare NO_2 concentrations in ambient air in areas of different human activities and population density in Chiang Mai City using NO_2 test kit and spectrophotometry.