สารกลุ่มคาร์บอนิลในบรรยากาศของกรุงเทพมหานครที่เกิดจากการใช้น้ำมันแก๊สโซฮอล์

นางเดซี่ หมอกน้อย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตร์ดุษฎีบัณฑิต
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บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

CARBONYL COMPOUNDS IN BANGKOK AMBIENT AIR ASSOCIATED WITH GASOHOL

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A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy Program in Environmental Management
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Thesis Title	Carbonyl Compounds in Bangkok Ambient Air Associated with Gasohol
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เดรี่ หมอกน้อย: สารกลุ่มคาร์บอนิลในบรรยากาศของกรุงเทพมหานครฯที่เกิดจากการใช้น้ำมันแก๊สโซฮอล์ (CARBONYL COMPOUNDS IN BANGKOK AMBIENT AIR ASSOCIATED WITH GASOHOL) **อ. ที่ปรึกษาวิทยานิพนธ์หลัก: *รศ. ดร.พจนีย์* ขุมมงคล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม อ. *ดร.ทรรศนีย์* พฤกษาสิทธิ์,** 182 **หน้า**

การวิจัยนี้ได้ดำเนินการเพื่อศึกษาสารกลุ่มคาร์บอนิลในบรรยากาศของกรุงเทพมหานคร อันเนื่องจากการใช้น้ำมันแก๊สโซฮอล์ โดยมีวัตถุประสงค์ เพื่อทราบชนิดและระดับความเข้มข้นของสารกลุ่มคาร์บอนิลในกรุงเทพมหานครฯ เพื่อศึกษาการกระจายในบรรยากาศของสารกลุ่มคาร์บอนิล และเพื่อทราบความเข้มข้นของสารกลุ่มคาร์บอนิล เปรียบเทียบกับจำนวนรถยนต์ที่ใช้น้ำมันแก๊สโซฮอล์ เพื่อบรรลุวัตถุประสงค์ดังกล่าว ได้มีการเก็บตัวอย่างอากาศจาก 10 **จุด ในกรุงเทพมหานคร ในปี** 2550 **ถึงปี** 2551 **โดยใช้ปั๊มเก็บตัวอย่างอากาศต่อกับหลอด เก็บตัวอย่างที่บรรจุสาร** 2,4 DNPH **อยู่ภายในหลอด และนำตัวอย่างมาสกัดและวิเคราะห์ ด้วยเทคนิค** HPLC **ตาม** US EPA Compendium Method TO-11A **ของสหรัฐอเมริกา ผลการศึกษาพบว่ามีสารกลุ่มคาร์บอนิลที่พบในบรรยากาศของกรุงเทพมหานคร จำนวน** 10 **ชนิด คือ สารฟอร์มาลดีไฮด์ สารอาเซทัลดีไฮด์ สารอะซีโตน สารโพรพิวนัลดีไฮด์ สารบิวทิรัลดีไฮด์ สารโครโทนัลดีไฮด์ สารเบนซัลดีไฮด์ สารไอโซวาราลดีไฮด์ สารวาราลดีไฮด์ และสารเฮ็กซานัลดีไฮด์ สารฟอร์มาลดีไฮด์ พบมากที่สุดในบรรยากาศของกรุงเทพมหานคร ในพื้นที่ริมถนน พบในช่วง** 5.14 – 17.2 **ไมโครกรัม/ลูกบาศก์เมตร (ค่าเฉลี่ย** 11.53 **ไมโครลกรัม/ลบ.ม.) ในพื้นที่อยู่อาศัย ในเวลาเดียวกันมีความเข้มข้นในช่วง** 3.06 – 19.9 **ไมโครกรัม/ลบ.ม. (ค่าเฉลี่ย 9.65 ไมโครกรัม/ลบ.ม.) ความเข้มข้นของสารอาเซทัลดีไฮด์ ในพื้นที่ริมถนนอยู่ในช่วง** 1.59 – 7.95 **ไมโครกรัม/ลบ.ม. (ค่าเฉลี่ย** 3.51 **ไมโครกรัม/ลบ.ม.) ในพื้นที่อยู่อาศัย ความเข้มข้นอยู่ในช่วง** 1.07 – 8.05 **ไมโครกรัม /ลบ.ม.) (ค่าเฉลี่ย** 3.11 **ไมโครกรัม/ลบ.ม.) สารกลุ่มคาร์บอนนิล อื่นๆ ที่พบในกรุงเทพมหานคร มีความเข้มข้นต่ำ ในการศึกษานี้พบว่าในเวลาที่มีการจราจรหนาแน่น ความเข้มข้นของสารฟอร์มัลดีไฮด์ และสารอะเซทัลดีไฮด์เพิ่มขึ้น ในเวลากลางคืน ความเข้มข้นของสารกลุ่มนี้ลดลงเนื่องจากการลดลงของแหล่งกำเนิด และจากการคำนวนความสัมพันธ์ระหว่างความเข้มข้นของสารฟอร์มาลดีไฮด์ในพื้นที่ริมถนนกับจำนวนรถยนต์พบว่ามีความสัมพันธ์ที่ดี** ($R^2 = 0.977$) **เช่นเดียวจากการคำนวนความสัมพันธ์ระหว่างความเข้มข้นของสารอาเซทัลดีไฮด์ในพื้นที่ริมถนนกับจำนวนรถยนต์พบว่ามีความสัมพันธ์ที่ดี** ($R^2 = 0.9256$)

สาขาวิชา การจัดการสิ่งแวดล้อม **ลายมือชื่อนิสิต** เดชี่ หมอกน้อย

ปีการศึกษา 2551 **ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก**

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

4789700120: MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: Carbonyl compounds, formaldehyde, acetaldehyde, carcinogenic compound

DAISY MORKNOY: CARBONYL COMPOUNDS IN BANGKOK AMBIENT AIR ASSOCIATED WITH GASOHOL: THESIS ADVISOR: ASSOCIATE PROFESSOR POJANIE KHUMMONGKOL, THESIS CO-ADVISOR: TASSANEE PRUEKSASIT, Ph.D., 182 pp.

This study has been conducted to focus on carbonyl compounds in Bangkok associated with gasohol. The objectives of the study were: to identify and quantify the carbonyl compounds present in urban air; to study the spatial distribution of carbonyl compounds in Bangkok urban area; and to determine the concentration of carbonyl compounds in relation to traffic density. In order to meet these objectives, ambient air samples were collected at 10 sites in Bangkok during 2007 to 2008, by using active cartridge sampler containing 2,4 DNPH and samples were extracted and analyzed using HPLC technique utilizing Compendium Method TO-11A of the US EPA as guideline. The results of the study indicated that there were 10 prevalent carbonyl compounds found both at the roadside and residential areas in Bangkok namely; formaldehyde, acetaldehyde, acetone, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, and hexanaldehyde. Formaldehyde was abundant in Bangkok ambient air especially in the roadside areas which ranged from 5.14 to 17.2 μg/m³ (average 11.53 μg/m³) while, in the residential areas during the same period ranged from 3.06 to 19.9 μg/m³ (average 9.65 μg/m³). The concentration of acetaldehyde in roadside areas in Bangkok during the same period ranged from 1.59 to 7.95 μg/m³ (average 3.51 μg/m³) while at the residential areas the concentration of this compound, ranged from 1.07 to 8.05 μg/m³ (average 3.11 μg/m³). Concentration levels of other carbonyl compounds in Bangkok were low. It was also found that at the roadside areas, during high traffic density the concentration of formaldehyde and acetaldehyde increased. The correlation between formaldehyde concentration and car density was calculated which indicated good correlations (R^2= 0.977). The correlation between acetaldehyde concentrations in the roadside area and car density was also calculated, and the (R^2= 0.9256), which indicated good correlation.

Field of Study: Environmental Management
Academic year 2008

Student's signature Daisy Morknoy
Advisor's signature Pojanie
Co-advisor's signature T Prueksasit

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CHAPTER I
INTRODUCTION

1.1 Rationale Background

Thailand has a few natural energy resources, and the fuel requirement was rapidly increasing along with the growth of the economy and industry therefore, fuel and energy supply has been an important issue in country because Thailand imports 90% total amount of petroleum used each year. In 1997, the retail price of gasoline began to increase when Thailand’s economy crashed, causing the exchange rate to become unstable. Moreover, OPEC decreased their oil production while the energy use rate especially oil, was still increasing. In 1999, Thailand lost more than 1,680 million by importing oil. These problems prompted the government to consider finding new sources of fuel and energy in the country to compensate the importation of oil. The Ministry of Energy (MOEN) promoted and supported the nationwide use of alternative fuels such as LPG, CNG, and gasohol to replace all conventional gasoline and diesel with biodiesel. There are many reasons for Thailand to pursue an ethanol program designed to reduce dependence on fossil fuels in the transportation sector. According to the policy, there are potential positive benefits of such program such as relief trade balance burdens due to heavy reliance on foreign oil, use of potentially carbon neutral fuel, future national security, and rural economic development. Such incentives have encouraged the Thai government to consider ethanol production as a realistic opportunity to accomplish these goals. (Ministry of Industry, A Study of Feasibility of Promotion on Ethanol Production Project, 2000). Thailand’s aim to expand the current production capacity to a large-scale industry capable of replacing at least 10% of foreign gasoline by volume. At present, the regular 95 octane-benzene was completely replaced with gasohol 95 since January 2007, and is already increasingly difficult to find regular 95 gasoline at gas stations. The regular 91 octane-benzene is allowed to be sold for some more years, but to be replaced with gasohol 91 by 2012. Biodiesel (B5) is now widely used in Thailand especially in the transportation sector. At present, the use of gasohol has reached more than 6.5 million liters/day. Likewise, the production of biodiesel has been initiated and would reach sales of more than 52 million liters/day. As part of the government's policy, the MOEN and the world's leading car manufacturers initiated a meeting on March 9, 2005 to assure that the use of gasohol would not damage the car engines and to inform car users that they can immediately use gasohol without making any engine modification. To promote gasohol usage to car owners, the price of gasohol was set at a lower price than the 95 or 91octane-benzene. In 1981, the project on pilot scale of power alcohol from cassava as an alternative source of energy was entrusted to the Thailand Institute of Scientific and Technological Research (TISTR) and the Ministry of Science, Technology and Environment by the cabinet's approval. (Thailand Institute of Scientific and Technological Research, 1983). In 1985, when His Majesty the King Bhumibol Adulyadej foresaw that Thailand might experience oil shortage, as well as low prices for agricultural products. Therefore, has again initiated a personal project at Chitralada Gardens to study the use of sugarcane to produce ethanol, which is then mixed with gasoline to produce gasohol. Experiments have been conducted with vehicles as part of the Chitralada project since 1994. Test with both small and large engines all yielded good results in the testing center and on the road.

Countries all over the world have produced ethanol for use in the transportation and industrial sector for several decades. These countries including Thailand were exploring the implementation of large-scale fuel ethanol programs. Brazil however, is the only country until this date that operates a nationwide fuel ethanol program capable of replacing substantial amount of gasoline. Ethanol blended fuels are now used in Europe, Japan, Philippines, Canada, and North America. Brazil in particular, has developed cars that used up to 25 percent ethanol, and recently 100% ethanol has already been used in about 14% of Brazil's total car population. Brazilian drivers can fill up with ethanol at 29,000 filling stations throughout the country, while USA have about 600 gasohol stations that sell the E85 fuel blended at 85% ethanol and 15% gasoline. Thailand have about 4,149 gasohol filling stations of E10 throughout the country.

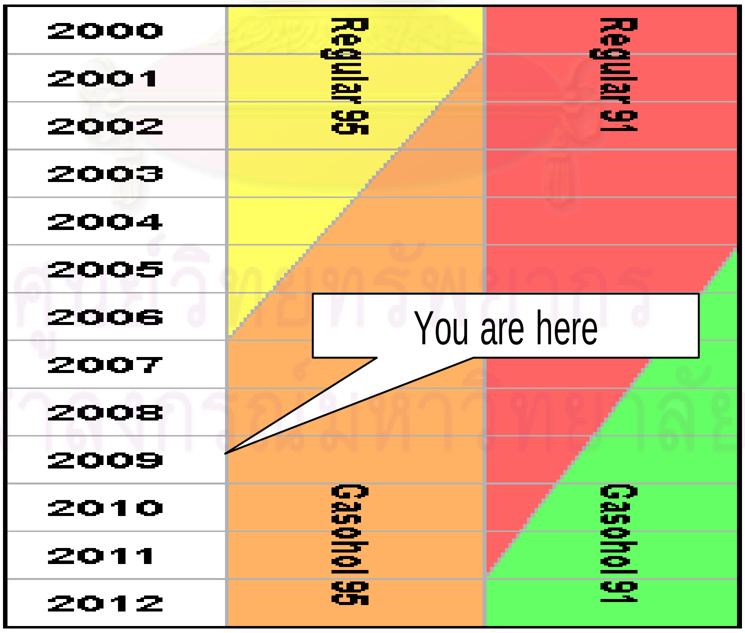

Figure 1.1 Gasohol Policy in Thailand.

Ethyl alcohol has long been used as an automotive fuel in two ways: First, it replaces gasoline outright in a somewhat modified internal combustion engine; and secondly, it is an effective "octane booster" when mixed with gasoline in blends of 10 to 30 percent and requires no engine modification. These blends achieve the same octane boosting (or anti-knock) effects as petroleum-derived aromatics like benzene or metallic additives like tetraethyl lead. Many people are familiar with Gasohol, a popular fuel blend in the American Midwest in the late 1970s, which was a blend of ten percent ethyl alcohol and gasoline. While ethanol, has many attractive qualities however, adding ethanol to gasoline in small amount increases the overall level of hydrocarbon emissions. The ethanol can be added to gasoline at levels as high as 2.1% oxygen without significantly increasing NOx levels, but above that point, NOx levels can increase somewhat. For example, the US Environmental Protection Agency (EPA) test data on over 100 cars indicates that oxygen levels of 2.7% or more could increase NOx emissions by 3–4%. Most studies found that MTBE increases formaldehyde emissions (Hood and Farina, 1995), acetaldehyde emissions increases greatly with ethanol. Although the potential positive benefits of ethanol are well known, a debate lingers among members of scientific communities, industry, and government as to the extent of these benefits. In some cases ethanol blended fuel can be proven as an environmental disaster if a proper assessment of the local environment is not performed. It is known that ethanol burned on vehicles, depending on the characteristics of the engine, can produce excess acetaldehyde. It is also known that under certain circumstances, acetaldehyde can cause significant increase in ground level ozone. What is not known is the effects of this excess acetaldehyde will have on the atmosphere of Thailand, especially Bangkok Metropolitan Region (BMR).

Combustion of ethanol in an internal combustion engine yields many of the products of incomplete combustion that are produced by gasoline and significantly larger amounts of formaldehyde and related species such as formalin, acetaldehyde, etc. (California Air Resources Board, 1989). This leads to a significantly larger photochemical reactivity that generates much more ground level ozone (Lowi A.et..al., 1990). This data has been assembled into The Clean Fuels Report comparison of fuel emissions and shows that ethanol exhaust generates 2.14 times as much ozone as does gasoline exhaust.

Table 1.1 Biofuel Refueling Stations in Thailand

Gasohol Station	4,149	Gasohol 95 Stations	3,530
		Gasohol 91 Stations	619
Bio-diesel B5 Stations	698	LPG Stations	256
Palm Diesel Stations	4	CNG Stations	115

Source: Ministry of Energy, 2008

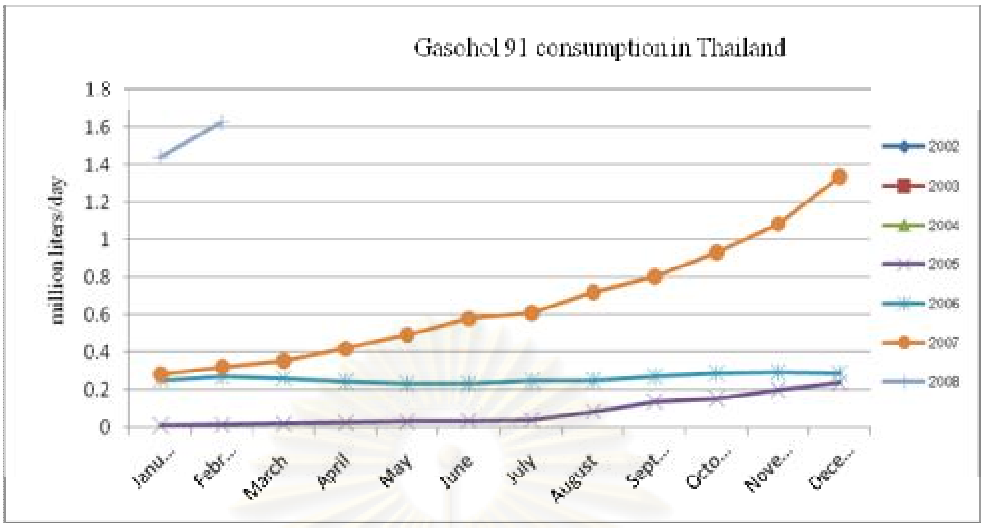

Figure 1.2 Consumption of gasohol 91 in Thailand

Formaldehyde decomposes into methanol and carbon monoxide at temperatures above 150◦C, though uncatalysed. Formaldehyde decomposition is slow at temperatures below 300◦C. Under atmospheric conditions, formaldehyde is readily photo-oxidized by sunlight to carbon dioxide. It reacts relatively quick with trace substances and pollutants in the air, and its half-life in urban under the influence of sunlight, is short. In the absence of nitrogen dioxide, the half-life of formaldehyde is approximately 50 minutes during the day; and in the presence of nitrogen dioxide, it is about 35 min.

Photo-oxidation of acetaldehyde occurs in the atmosphere through various mechanisms, such as the reaction with hydroxyl radicals, ozone, hydroperoxyl radicals and nitrate radicals. On the basis of the rate constant for each of the reactions and the concentration of the reactants, the reaction with the hydroxyl radical is considered to be the most important (Atkinson, R.,1990). Factors influencing acetaldehyde's atmospheric lifetime, such as time of day, sunlight intensity and temperature, also include those affecting the availability of hydroxyl radicals and nitrate radicals. The atmospheric half-life of acetaldehyde, based on hydroxyl radical reaction rate constants, is calculated to be less than six hours (Canadian Environmental Protection Act, 1999). Furthermore, formaldehyde and acetaldehyde were determined by US. EPA as carcinogenic compounds. Therefore, their presence in the ambient air may posses a treat to human health. The final report on the identification of formaldehyde as a toxic contaminant which was prepared by the California Environmental Protection Agency's Air Resources board and the Office of Environmental Health Hazard Assessment (OEHHA) on March 1992, which stated that the upper bound risk of contracting cancer from continuous exposure to Formaldehyde at 1 ppbv to range from 0.3 to 40 x 10^{-6} ppbv (0.25 to 33 x 10^{-6} $\mu g/m^3$). This corresponds that 1 to 40 potential excess cancers occur among a million people continuously exposed to 1 ppbv formaldehyde over a 70-year lifetime. The OEHHA also recommend that the unit risk for acetaldehyde is 4.8 x 10^{-6} ppbv (2.7 x 10^{-6} $\mu g/m^3$) be considered the best value of the upper bound of risk. This unit risk stated that with a lifetime exposure to 1 ppbv acetaldehyde over a 70-year lifetime. would yield 4.8 excess potential cancer cases per million people.

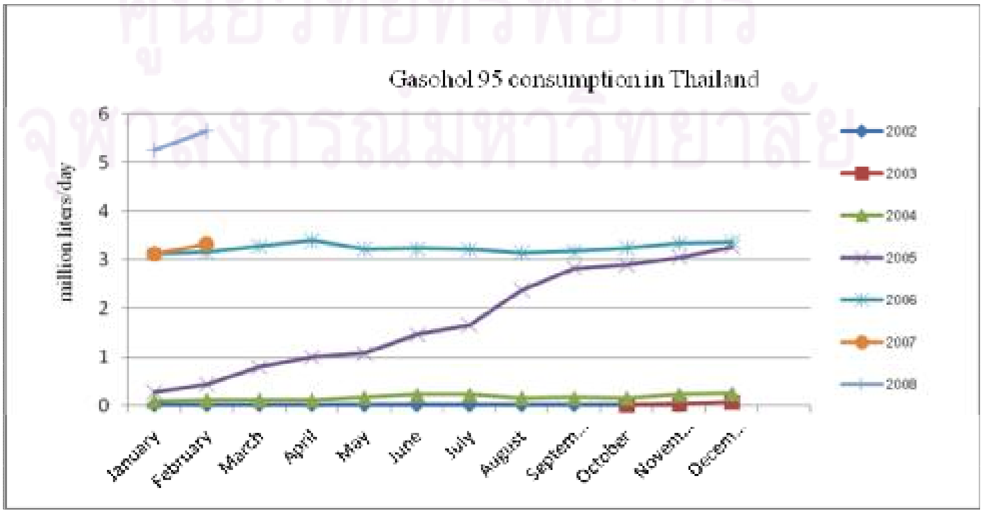

Figure 1.3 Consumption of gasohol 95 in Thailand

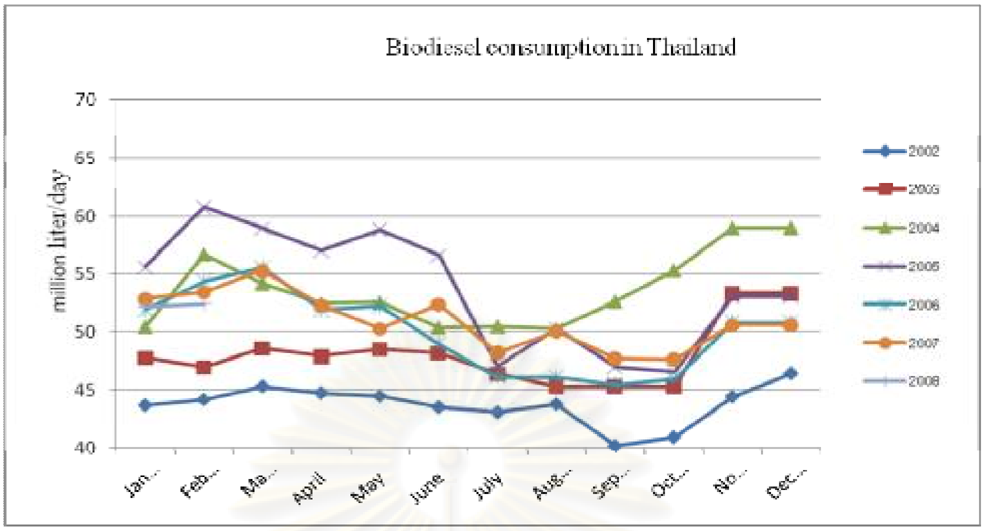

Figure 1.4 Consumption of biodiesel in Thailand

A kinetic trajectory model (OZIPW) was done by Bangkok Metropolitan Region (BMR) to explore the impact of different motor vehicle or fuel policy initiatives on ozone formation in the atmosphere of BMR related to ethanol use. There was a high probability that ethanol use in Thailand will increase ambient concentration of ground-level ozone in the short term. The addition of aldehydes in the model resulted in increase of ozone production in the atmosphere of Bangkok as seen in result of the OZIPW model. The most susceptible days to increase ozone from ethanol use, are low ozone days, but the extent of these increases are still unknown. The results of low ozone day showed a large increase of ozone with the addition of 20% aldehydes to the BMR atmosphere, and even greater change if total VOCs were reduced. It was also observed that the additional increase in aldehydes to the model (such as from a change of MTBE 7.5% to ethanol 7.5%) gave significant rise in ozone (Zhang-B.N. et al., 2002).

Ultimately, the ethanol program in Thailand must be beyond the definition of feasibility and sustainability. The sustainability of ethanol production program incorporates technological and economic realities with social and environmental necessities. Even if the ethanol program proves feasible technologically and economically, the health of Thailand's society and environment are crucial to maintain its long term success. Therefore, the establishment of Air Quality Standards for toxic air pollutants, and constant monitoring and evaluation of the status of carbonyl compounds in the environment is very important to go along with the ethanol program, in order to achieve and maintain sustainability.

The use of ethanol blended gasoline in transportation sector has been proposed as an alternative fuel strategy that might improve air quality minimizing dependence on fossil fuels. In an attempt to reduce urban benzene, 1,3butadiene, and carbon monoxide concentration levels, the Thai government is currently mandating the use of ethanol blended gasoline. It is not clear that this ethanol blended fuel will help improve air pollution in Thailand. In fact, the use of this fuel may lead to increased level of aldehydes especially formaldehyde, acetaldehyde and acrolein. Although these pollutant are not currently regulated in Thailand, their potential health and environmental impacts must be considered when assessing the impacts of alternative fuels on air quality in Thailand.

1.2 Objectives of the Study are:

This study aims to develop a baseline study for carbonyl compounds in Bangkok's ambient air associated with gasohol. There were three specific objectives carried out namely:

1. To identify and quantify the carbonyl compounds present in urban air.

2. To study the spatial distribution of carbonyl compounds in Bangkok urban area.
3. To determine the concentration of carbonyl compounds in relation to traffic density

1.3 Scope of the Study

This study was generally focused on Bangkok urban area and the sampling sites were mainly selected from the air quality monitoring stations of the Pollution Control Department, Bangkok. For the analysis of carbonyl compounds the researcher utilized the Compendium Method TO-11A as guideline which focused on 15 carbonyl compounds. However, much emphasis has been given to formaldehyde and acetaldehyde because these compounds were related to gasohol fuel. Moreover, these compounds are toxic and pose public health risks. These two compounds also act as photochemical precursors to free radicals and, therefore, play an important role in ground level ozone formation. Carbonyl compounds are emitted from sources or formed in the atmosphere from atmospheric oxidation of hydrocarbons, incomplete combustion carbonaceous material and fossil fuels. Furthermore, these compounds were found prevalent in Bangkok's ambient air, and some were classified as carcinogenic by the US Environmental Protection Agency, IARC and Office of the Environment Health and Hazard Assessment.

1.4 Benefits from the Study

Carbonyl compounds especially formaldehyde and acetaldehyde are compounds that were stated by the Office of the Environmental Health Hazard Agency (OEHHA) and U.S. Environmental Protection Agency (US EPA) as carcinogenic compounds. After completing this research, the researcher expect to obtain reliable data to propose to the Pollution Control Department as a supplemental data for the establishment of Air Quality Standards for Toxic Air Pollutants in Thailand, to protect the health of the people especially the vulnerable group. The data acquired is also very useful as baseline information for carbonyl compounds in relation to the use gasohol as an alternative fuel in Thailand. Moreover, this study will also serve as guideline for the study of other alternative fuels such as biodiesel, CNG, and others.

CHAPTER II
LITERATURE REVIEW

2.1 Current Ambient Air Quality in Bangkok

In 1992, the Pollution Control Department (PCD) started to build up a nationwide ambient air quality monitoring network and meteorological monitoring network. The networks were gradually installed over several phases, and were completed in 1996. The ambient air quality monitoring network consists of 53 automated ambient air quality monitoring stations located throughout the country. Various ambient air pollutants were measured such as CO, NOx, SO_2, O_3, TSP, PM_{10}, Pb, HC, and H_2S. Results of ambient air quality monitoring for more than 10 years indicate that the air pollutants of greatest concern in Bangkok are SPM, especially PM_{10} and CO which were mostly emitted by the transport sector. Air pollution in Bangkok due to high concentration of SPM was among the highest priority problems (Wangwongwatana, S., et al., Air Pollution Management in Thailand). High concentration and frequent exceed of ambient air quality standards for TSP, PM_{10}, and CO especially along the major roads in Bangkok, were high enough to result in significant adverse health impacts to the people.

Research in cities throughout the world indicates that current levels of public exposure to airborne particulate matter are associated with premature mortality and respiratory-related illness. Particulate air pollution includes solid and liquid particles directly emitted into the air such as diesel soot, road dust from the transportation sector, agricultural dust, or particles resulting from construction or manufacturing processes. Particulate air pollution is also produced through photochemical reactions among pollutant gases such as sulfur dioxide or nitrogen oxides that are a byproduct of fuel combustion. The illnesses associated with airborne particulate matter range from severe acute and chronic illnesses such as asthma attacks and chronic bronchitis to mild acute symptoms such as coughing, wheezing, and congestion. The daily mortality study examined the relationship between daily fluctuations in PM10 and the number of deaths each day in Bangkok based on available death certificate, PM10, and weather data. This analysis determines the increased mortality risk, if any, associated with short-term fluctuations in PM_{10} concentrations, but does not necessarily reflect risks associated with long-term exposures. Studies in many cities around the world have found that increases in particulate matter concentrations on a given day are associated with increases in mortality within a few days thereafter. These associations have been observed even in locations where local air quality standards are met on most days. Available results from other cities suggest that on average, a day with a 30 mg/m^3 increase in PM_{10} concentrations (24-hour average) is associated with about 3% higher daily mortality. Like many other megacities in the world, the air pollution problem in Bangkok was associated mainly with the use of fuels in the transport sector. The government, therefore, started examining petroleum fuel specifications with the aim of reducing transport emissions as one of the several measures to improve air quality in Bangkok.

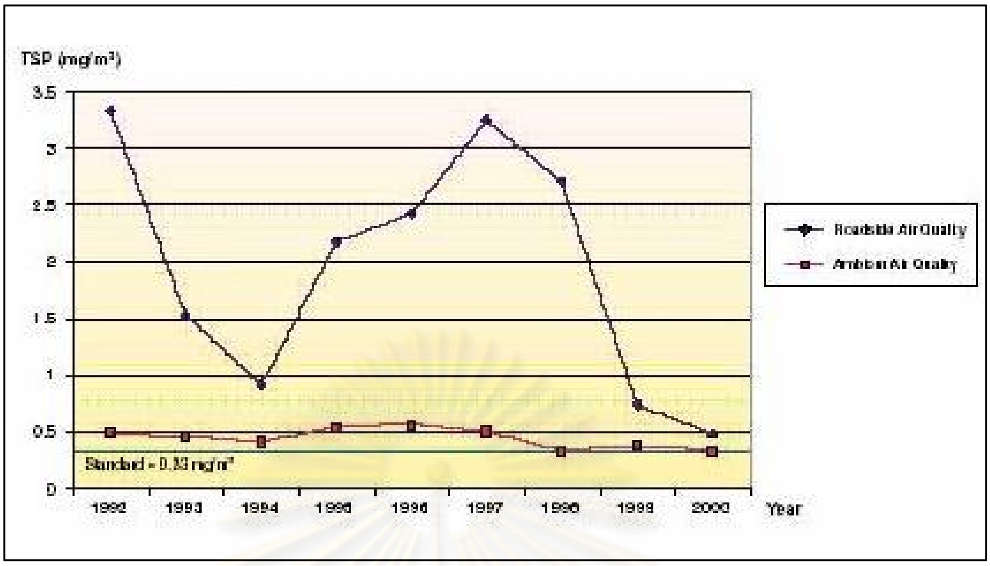

Figure 2.1 Average Concentration of Total Suspended Particles (TSP) in Bangkok (1992- 2000)

Source: Pollution Control Department, 2000

2.2 Thailand’s Policy on Alternative Energy by Ethanol

Thailand has already developed a detailed, supporting policy for its ethanol program. On December 26, 2000, the Thai cabinet approved promotions and supporting measures on the production of and utilization of ethanol fuels, as proposed by the Ministry of Industry. According to the policy the government will support the establishment of ethanol factories according to prescribed promotions and other various measures. This project will not only ease dependence on importation of oil additives, but will also potentially solve current air pollution problems, while developing new markets for selected agricultural crops. Hopefully, these measures will provide stability in both energy supply and economy of the country, The Ministry of Energy had also determined the energy strategies for the country’s competitiveness, which had been approved by the cabinet on September 2, 2003. One of these strategies is the sustainable alternative energy development that had set the target on increasing the proportion of commercial renewable energy generation from 0.5 percent in 2001 up to 8 percent by 2002. Biofuel development, from ethanol and bio-diesel, is a goal under the plan of increasing the proportion of renewable energy use. Ministry of Energy, by DEDE, had established a Gasohol Strategy to propose in the Joint Meeting between the Ministry of Energy, and the Ministry of Industry and finally proposed to the Cabinet on December 9, 2003. The Ministry of Energy had set the target on using ethanol to replace Methyl Tertiary Butyl Ester (MTBE) in gasoline 95 by 1 million L/day by 2006 and to use ethanol to replace MTBE in gasoline 95 and gasoline 91 for 3 million L/day by the year 2011. The Ministry of Energy also proposed the cabinet to agree on reducing the Oil Fund burden on April 19, 2005 by proposing gasohol use promotion scheme as well as to speed up in increasing the gas stations from 800 to 4000 stations throughout the country by the end of 2005. The government also emphasized on the use of gasohol in all vehicles of government and of state enterprise to comply with the cabinet resolution dated December 9, 2003. A requirement on the 431 gas stations located within the government and state enterprise campuses to change for selling on gasohol. The Ministry of Energy had also determined the measures to support and promote using biofuel, especially gasohol by increasing the pricing difference between gasoline and gasohol and increasing the remittance to the Oil Fund. The Thai Government has formulated a two- phase gasohol (gasoline-ethanol blend) program. In Phase 1 (2004-2006), in addition to the three ethanol plants currently operating, three others are scheduled to come on-stream by the end of 2006, and this will increase the production capacity to 1.155 million liters/day. For Phase 2 (2007-2012), the Government awarded license to 18 new biodiesel plants, and this will bring the total installed capacity to 3 million liters/day by 2012. Of the 18 new plants in Phase 2, 14 will use molasses as feedstock and the remaining four will be cassava-based. Thailand's gasoline demand is estimated to be 30 million liters/day by 2012, and so there will be sufficient ethanol for blending in E10 gasohol (10% ethanol in gasoline) to meet the entire national daily demand (27 million liters of regular gasoline plus 3 million liters of ethanol). By 2012, the 91 octane regular gasoline will be replaced by E10 gasohol, which has an octane rating of 95. The Government is providing the necessary infrastructure for ethanol blending and gasohol distribution. The sustained availability of feedstock (sugarcane/molasses, cassava) for ethanol manufacture is of critical importance to the success of the gasohol program. Thailand is by far the largest producer of sugarcane in South-East Asia. Sugarcane production peaked at 74.3 million tons in 2003 but fell to 65.0 million tons in 2004 and 49.6 million tons in 2005 owing to drought conditions. Even so, the sugar produced (5 million tons in 2005) is greatly in excess of domestic requirements (about 2 million tons annually), and so Thailand is a major exporter of sugar and molasses. Through the allocation of a portion of the sugarcane grown to direct ethanol manufacture, the ethanol production capacity can be further increased. Thailand is well positioned to become the dominant ethanol producer in Asia(Ministry of Energy,). Thailand is Asia’s largest producer of cassava, with an average output of 20 million tons a year. After domestic consumption and export requirements have been met, about 4 million tons are available annually; and at a conversion rate of 6 kg cassava root per liter of ethanol, this will yield 1.8 million liters of ethanol per day. The biodiesel industry is in its infancy in Thailand but is poised for rapid growth. Diesel consumption is currently at 50 million liters/day and is expected to rise to 85 million liters/day by 2012. The Government plans to have an installed biodiesel production capacity of 8.5 million liters/day by 2012 so that B10 (10% biodiesel in diesel) can meet the national diesel requirements. A key element of the Government's strategic plan for biodiesel is plantation development for the vegetable oil crops to be used as feedstock palm oil and Jatropha. Palm oil is the world's most productive vegetable oil crop, and being the northern neighbor of the world's largest palm oil producer, Malaysia, Thailand has the right climatic and soil conditions for large-scale palm cultivation. The Government plans to develop palm plantations totaling 4 million rai (0.7 million hectares), which will yield 4.8 million liters/day of biodiesel. In addition, palm plantations covering 1 million rai in area will be developed in a neighboring country, most likely Malaysia, and this will lead to an additional biodiesel production capacity of 1.2 million liters/day. Finally, the Government plans to cultivate more palm and Jatropha to bring biodiesel production to 2.5 million liters/day, as a result of which the total daily biodiesel production will be 8.5 million liters by 2012. The Government has created an enabling environment for biofuels development. The National Biofuels Committee is responsible for policy direction, strategy planning and implementation. It is supported by the ministries of finance, agriculture, industry and energy. Financing and project development mechanisms have been set up through Special Purpose Vehicles (SPV) and financial institutions for successful project implementation. By 2012, the ethanol and biodiesel programs will save the national economy by $325 million and $675 million, respectively, each year.

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2.3 Facts About Ethanol

Ethanol has been used by human since prehistory as the intoxicating ingredient of alcoholic drinks. Dried residues on 9000 year old pottery found in China imply the use of alcoholic drinks even among the Neolithic people. Its isolation as a relatively pure compound was first achieved by Persian alchemist, Zakarya Rzi (Rhazes), who was renowned for his perfected methods of distillation and extraction. Other chemists who contributed to the development of distillation techniques during the Abbasid caliphate, other than Razi, include Jabiribn Hayyan Geber and Al-Kindi Alkindus. In 1796, Johann Tobias Lowitz obtained pure ethanol by filtering distilled ethanol through activated charcoal. Antoine Lavoisier described ethanol as a compound of carbon, hydrogen, and oxygen, and in 1808 Nicolas-Théodore de Saussure determined ethanol's chemical formula. Fifty years later, Archibald Scott Couper published the structural formula of ethanol, which placed ethanol among the first chemical compounds to have their chemical structure determined. Ethanol was first prepared synthetically in 1826 through the independent efforts of Henry Hennel in Great Britain and S.G. Sérullas in France. In 1828, Michael Faraday prepared ethanol by acid-catalyzed - catalyzed hydration of ethylene, a process similar to that which is used today for industrial ethanol synthesis . Ethanol was used as lamp fuel in the United States as early as 1840, but a tax levied on industrial alcohol during the Civil War made this use uneconomical. This tax was repealed in 1906, and from 1908 onward Ford Model T automobiles could be adapted to run on ethanol (Dipardo, J., 2007).With the advent of Prohibition in 1920 though, sellers of ethanol fuel were accused of being allied with moonshiners, and ethanol fuel again fell into disuse until late in the 20th century.

Ethanol is a volatile, flammable, colorless liquid that has a strong characteristic odor. It burns with a smokeless blue flame that is not always visible in normal light. The physical properties of ethanol stem primarily from the presence of its hydroxyl group and the shortness of its carbon chain. Ethanol’s hydroxyl group is able to participate in hydrogen bonding, rendering it more viscous and less volatile than less polar organic compounds of similar molecular weight. Ethanol is a versatile solvent, miscible with water and with many organic solvents, including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether, ethylene glycol, glycerol, nitromethane, pyridine, and toluene. It is also miscible with light aliphatic hydrocarbons, such as pentane and hexane, and with aliphatic chlorides such as trichloroethane and tetrachloroethylene. Ethanol's miscibility with water contrasts with that of longer-chain alcohols (five or more carbon atoms), whose water miscibility decreases sharply as the number of carbons increases Mixtures of ethanol and water that contain more than about 50% ethanol are flammable and easily ignited. An alcohol stove has been developed in India which runs on 50% ethanol/water mixture. (Rajvanshi, A.K., 2007). Alcoholic proof is a widely used measure of how much ethanol (i.e., alcohol) such a mixture contains. In the 18th century, proof was determined by adding liquor (such as rum) to gunpowder. If the gunpowder still just exploded, that was considered to be 100 degrees proof that it was good liquor, hence it was called 100 degrees proof.

Ethanol's hydroxyl causes the molecule to be slightly basic, it is almost neutral like pure water. The pH of 100% ethanol is 7.33, compared to 7.00 for pure water. Ethanol can be quantitatively converted to its conjugate base, the ethoxide ion ($CH_3CH_2O^-$), by reaction with an alkali metal such as sodium.

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2,$$

Or a very strong base such as sodium hydride:

$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2$$

This reaction is not possible in an aqueous solution, as water is more acidic, so that hydroxide is preferred over othoxide formation.

Under acid-catalyzed conditions, ethanol reacts with carboxylic acids to produce ethyl esters and water:

$$RCOOH + HOCH_2CH_3 \longrightarrow RCOOCH_2CH_3 + H_2O$$

For this reaction to produce useful yields it is necessary to remove water from the reaction mixture as it is formed. Ethanol can also form esters with inorganic acids. Diethyl sulfate and triethyl phosphate, prepared by reacting ethanol with sulfuric and phosphoric acid respectively, are both useful ethylating agents in organic synthesis. Ethyl nitrite, prepared from the reaction of ethanol with sodium nitrite and sulfuric acid, was formerly a widely-used diuretic. Strong acid desiccants, such as sulfuric acid, cause ethanol's dehydration to form either diethyl ether or ethylene:

$$2\ CH_2CH_3OH \longrightarrow CH_3CH_2OCH_2\ CH_3 + H_2O$$

$$CH_3CH_2OH \longrightarrow H_2C{=}CH_2 + H_2O$$

Ethanol can be oxidized to acetaldehyde, and further oxidized to acetic acid. In the human body, these oxidation reactions are catalyzed by enzymes. In the laboratory, aqueous solutions of strong oxidizing agents, such as chromic acid or potassium permanganate, oxidize ethanol to acetic acid, and it is difficult to stop the reaction at acetaldehyde at high yield. Ethanol can be oxidized to acetaldehyde, without over oxidation to acetic acid, by reacting it with pyridinium chromic chloride The direct oxidation of ethanol to acetic acid using chromic acid is shown below:

$$C_2\ H_5OH\ + 2(O) \longrightarrow CH_3COOH + H_2O$$

The oxidation product of ethanol, acetic acid, is spent as nutrient by human body, as acetyl CoA where the acetyl group is spent as energy or used as biosynthesis.

When exposed to chlorine, ethanol is both oxidized and its alpha carbon chlorinated to form the compound, chloral.

$$4Cl_2 + C_2\,H_5OH \longrightarrow CCl_3 + CHO + 5HCl$$

Combustion of ethanol forms carbon dioxide and water:

$$C_2\,H_5OH(g) + 3O_2(g) \longrightarrow 2CO_2\,(g) + H_2O(1);$$

Ethanol is produced both as a petrochemical, through the hydration of ethylene, and biologically, by fermenting sugars with yeast. Which process is more economical is dependent upon the prevailing prices of petroleum and of grain feed stocks. Ethanol for use as industrial feedstock is most often made from ethanol is as a motor fuel and fuel additive. The largest national fuel ethanol industries exist in Brazil (gasoline sold in Brazil contains at least 25% ethanol-petrochemical feed stocks, typically by the acid-catalyzed hydration of ethylene, represented by the chemical equation below:

$$C_2\,H_4(g) + H_2O(g) \longrightarrow CH_3CH_2OH_{(1)}$$

Ethanol for use in alcoholic beverages, and the vast majority of ethanol for use as fuel, is produced by fermentation. The process of culturing yeast under conditions to produce alcohol is called fermentation. When certain species of yeast, most importantly, *Saccharomyces cerevisiae*, metabolize sugar in the absence of oxygen, they produce ethanol and carbon dioxide.

The chemical equation below summarizes the conversion of ethanol:

$$C_2\,H_{12}O_6 \longrightarrow 2CH_3CH_2OH + 2CO_2$$

Absolute or anhydrous alcohol generally refers to purified ethanol, containing no more than one percent water. Absolute alcohol not intended for human consumption often contains trace amounts of toxic benzene (used to remove water by azeotropic distillation). Consumption of this form of ethanol can be fatal over a short time period.

Generally this kind of ethanol is used as solvents for lab and industrial settings where water will disrupt a desired reaction. Pure ethanol is classed as 200 proof in the USA, equivalent to 175 degrees proof in the UK system.

The Brazilian production of ethanol is praised for the high carbon sequestration capabilities of the sugar cane plantations, thus making it a real option to combat climate change . Henry Ford designed the first mass-produced automobile, the famed Model T Ford, to run on pure anhydrous (ethanol) alcohol which he explained as "the fuel of the future". Today, however, 100% pure ethanol is not approved as a motor vehicle fuel in the U.S. Combustion of ethanol in an internal combustion engine yields many of the products of incomplete combustion that are produced by gasoline and significantly larger amounts of formaldehyde and related species such as formalin, acetaldehyde, etc. (California Air Resources Board, 1989). This leads to a significantly larger photochemical reactivity that generates much more ground level ozone. This data has been assembled into The Clean Fuels Report comparison of fuel emissions and shows that ethanol exhaust generates 2.14 times as much ozone as does gasoline exhaust. This issue has been formalized by the California Air Resources Board in 2008 by recognizing control standards for formaldehydes as an emissions control group like other conventional NOx and Reactive Organic Gases (Lowi, A. et al., 1990, Jones, T.T.M., 2008).

World production of ethanol in 2006 was 51 gigalitres (1.3×10^{10} US gal), with 69% of the world supply coming from Brazil and the United States. More than 20% of the Brazilian fleet of cars on the streets use 100% ethanol as fuel, which includes ethanol-only engines and flex-fuel engines. Flex-fuel engines in Brazil are able to work with all ethanol, all gasoline or any mixture of both. In the US flex-fuel vehicles can run on 0% to 85% ethanol (15% gasoline) since higher ethanol blends are not yet allowed.

Brazil supports this population of ethanol-burning automobiles with large national infrastructure that produces ethanol from domestically grown sugar cane. Sugar cane not only has a greater concentration of sucrose than corn (by about 30%), but is also much easier to extract. The bagasse generated by the process is not wasted, but is utilized in power plants as a surprisingly efficient fuel to produce electricity. The United States fuel ethanol industry is based largely on corn. The energy content of some energy fuels compared with ethanol is shown in Table 2.1.

Table 2.1 Energy content of some fuels compared with ethanol

Energy content of some fuels compared with ethanol.			
Fuel type	MJ/L	MJ/kg	Research octane number
Methanol	17.9	19.9	123
Ethanol	23.5	31.1	129
Liquefied natural gas	25.3	~55	
Autogas (LPG) (60% Propane + 40% Butane)	26.8	50.	
Aviation gasoline	33.5	46.8	
Gasohol (90% gasoline + 10% ethanol)	33.7	47.1	93/94
Regular Gasoline	34.8	[37]44.4	min. 91
Premium Gasoline			max. 95
Diesel	38.6	45.4	25
Charcoal, extruded	50	23	

The National Institute on Alcohol Abuse and Alcoholism maintains a database of alcohol-related health effects. Ethanol is a *central nervous system depressant* and has significant psychoactive effects in sublethal doses; for specifics, see effects of alcohol on the body by dose. Based on its abilities to change the human consciousness, ethanol is considered a drug. Death from ethyl alcohol consumption is possible when blood alcohol level reaches 0.4%. A blood level of 0.5% or more is commonly fatal. Levels of even less than 0.1% can cause intoxication, with unconsciousness often occurring at 0.3–0.4%. The amount of ethanol in the body is typically quantified by blood alcohol content (BAC), the milligrams of ethanol per 100 milliliters of blood. Small doses of ethanol generally produce euphoria and relaxation; people experiencing these symptoms tend to become talkative and less inhibited, and may exhibit poor judgment. At higher dosages (BAC > 100 mg/dl), ethanol acts as a central nervous system depressant, producing at progressively higher dosages, impaired sensory and motor function, slowed cognition, stupefaction, unconsciousness, and possible death. In America, about half of the deaths in car accidents occur in alcohol related crashes (Hingson, R., 2003). There is no completely-safe level of alcohol for driving, the risk of a fatal car accident rises with the level of alcohol in the driver's blood. However, most drunk driving laws governing the acceptable levels in the blood while driving or operating heavy machinery set typical upper limits of blood alcohol content (BAC) between 0.05% to 0.08%. (Hingston, R. 2003). The Table below summarizes the symptoms of ethanol consumption.

Table 2.2 Symptoms of ethanol consumption

Blood Alcohol Content (mg/dL)	Symptoms[82]
50	Euphoria, talkativeness, relaxation
100	Central nervous system depression, impaired motor and sensory function, impaired cognition
>140	Decreased blood flow to brain
300	Stupefaction, possible unconsciousness
400	Possible death
>550	Death

Main article: Alcohol metabolism

Ethanol within the human body is converted into acetaldehyde by alcohol dehydrogenase and then into acetic acid by acetaldehyde dehydrogenase. The product of the first step of this breakdown, acetaldehyde, is more toxic than ethanol. Acetaldehyde is linked to most of the clinical effects of alcohol. It has been shown to increase the risk of developing cirrhosis of the liver, multiple forms of cancer, and alcoholism. Ethanol is also classified as a teratogen. Ethanol is not a carcinogen. However, the first metabolic product of ethanol, acetaldehyde, is toxic, mutagenic, and carcinogenic. Also, ethanol's effect on the liver can contribute to immune depression.

2.4 Atmospheric Chemistry of Ethanol

The atmospheric chemistry of ethanol have already undergone extensive reviews by (Grosjean, 1997) and has summarized few studies of the atmospheric chemistry of alcohols. The only significant atmospheric reaction for ethanol is with OH radicals. Three possible initial reactions are:

$$C_2H_5OH + OH \longrightarrow CH_2CH_2OH + H_2O \qquad (1)$$

$$\longrightarrow CH_3CHOH + H_2O \qquad (2)$$

$$\longrightarrow CH_3CH_2O + H_2O \qquad (3)$$

The major reaction pathway of ethanol is Reaction 4 which involves H-atom abstraction from the weakest C-H bond. The reaction pathway that involves H-atom abstraction from the O-H bond (Reaction 5) is negligible under atmospheric conditions, and Reaction 3 is a minor pathway. The preferred IUPAC value for the reaction with the OH radical above is 3.2×10^{-12} $cm^3 molecule^{-1} s^{-1}$ at 298 K (Atkinson *et al.*, 1999a). Product studies showed that the major product from the reaction of ethanol with OH radicals is acetaldehyde with a formation yield of about 80%. The other possible minor products include formaldehyde and methyl nitrate (Grosjean, 1997). Once formed from the atmospheric reaction of ethanol with OH radicals, acetaldehyde is rapidly consumed by photolysis and by reaction with OH radicals. Photolysis leads to formation of CO and formaldehyde while reaction with the OH radical leads to PAN by the following process:

$$CH_3CHO + OH \longrightarrow CH_3CO + H_2O \qquad (4)$$

$$CH_3CO + O_2 \longrightarrow CH_3CO_3 \qquad (5)$$

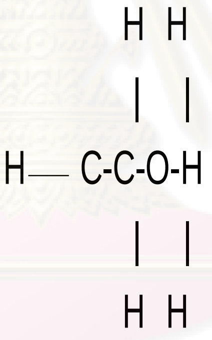
$$CH_3CO_3 + NO_2 \longrightarrow CH_3C(O)OONO_2 \quad (PAN) \qquad (6)$$

The acetyl (CH_3CO_3) radical also reacts with NO to form CH_3CO_2 and NO_2. In addition, PAN decomposes back to CH_3CO_2 and NO_2 in a reaction that increases at higher temperatures. Ambient concentrations of PAN are a function of ambient temperature, the NO_2-to-NO ratio, and the concentration of the acetyl radical precursor.

2.5 What are Oxygenates?

Oxygenates are hydrocarbons. They contain oxygen, which can not provide energy, but their structure provides a reasonable anti-knock value, thus they are good substitutes for aromatics, and they may also reduce the smog-forming tendencies of the exhaust gases.

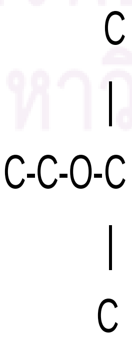
Ethanol



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$$

C_2H_5OH

Methyl tertiary butyl ether



$$C-C-O-\underset{C}{\overset{C}{C}}$$

$C_4H_9OCH_3$

Oxygenates can be produced from fossil fuels e.g. methanol (MeOH), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), or from biomass, e.g. ethanol(EtOH), ethyl tertiary butyl ether (ETBE)). Most oxygenates used in gasoline are either alcohols (Cx-O-H) or ethers (Cx-O-Cy), and contain 1 to 6 carbons. Oxygenates are added to gasoline to reduce the reactivity of emissions, but they are only effective if the hydrocarbon fractions are carefully modified to utilize the octane and volatility properties of the oxygenates. If the hydrocarbon fraction is not correctly modified, oxygenates can increase the undesirable smog-forming and toxic emissions. The major reduction in the reactivity of exhaust and evaporative emissions will occur with reformulated gasoline, due to be introduced in January 1995, in which the hydrocarbon fraction was significantly modified, and these gasoline are called "reformulated gasoline" (RFGs). Oxygenates do not necessarily reduce all individual exhaust toxins, nor are they intended to. The change to reformulated gasoline requires oxygenates, but also that the hydrocarbon composition must be significantly more modified than the existing oxygenated gasoline to reduce unsaturates, volatility, benzene, and the reactivity of emissions. MTBE works by retarding the progress of the low temperature or cool-flame reactions, consuming radical species, particularly OH radicals and producing isobutene. The isobutene in turn consumes additional OH radicals and produces unreactive, resonantly stabilized radicals such as allyl and methyl allyl, as well as stable species such as allene, which resist further oxidation.

Oxygenates that are added to gasoline function in two ways. Firstly they have high blending octane, and so can replace high octane aromatics in the fuel. These aromatics are responsible for disproportionate amounts of CO and HC exhaust emissions. This is called the "aromatic substitution effect". Oxygenates also cause engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emissions of CO (2% oxygen can reduce CO by 16%) and HC (2% oxygen can reduce HC by 10%)[7]. Oxygen in the fuel can not contribute energy, consequently the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in combustion efficiency that oxygenates provide on some engines usually do not completely compensate for the oxygen. The major concern with oxygenates is no longer that they may not be effective at reducing atmospheric pollution, but that their greater water solubility, and very slow biodegradability, can result in groundwater pollution that may be difficult to remove.

2.6 Carbonyl Compounds

In organic chemistry, a carbonyl group is a functional group composed of a carbon atom double-bonded to an oxygen atom. In aldehydes, the carbonyl group is on the "end" of a carbon chain, while in ketones, it is in the "middle" of a carbon chain. The double bond in the carbonyl group is very susceptible to chemical reactions. Carbonyl groups can be reduced by reaction with hydride reagents such as $NaBH_4$ and $LiAlH_4$, or catalytically by hydrogen and a catalyst such as copper chromite, Raney nickel, rhenium, ruthenium or even rhodium. Ketones give secondary alcohols; aldehydes, esters and carboxylic acids give primary alcohols. Carbonyls can be alkylated by nucleophilic attack by organometallic reagents such as organolithium reagents and Grignard reagents. Carbonyls also be alkylated by enolates as in aldol reactions. Carbonyls are also the prototypical groups with vinylogous reactivity, e.g. the Michael reaction where an unsaturated carbon in conjugation with the carbonyl is alkylated instead of the carbonyl itself.

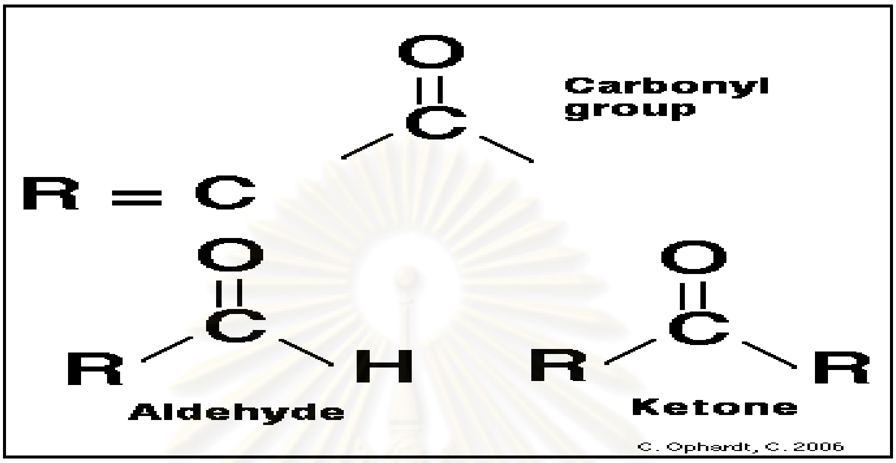
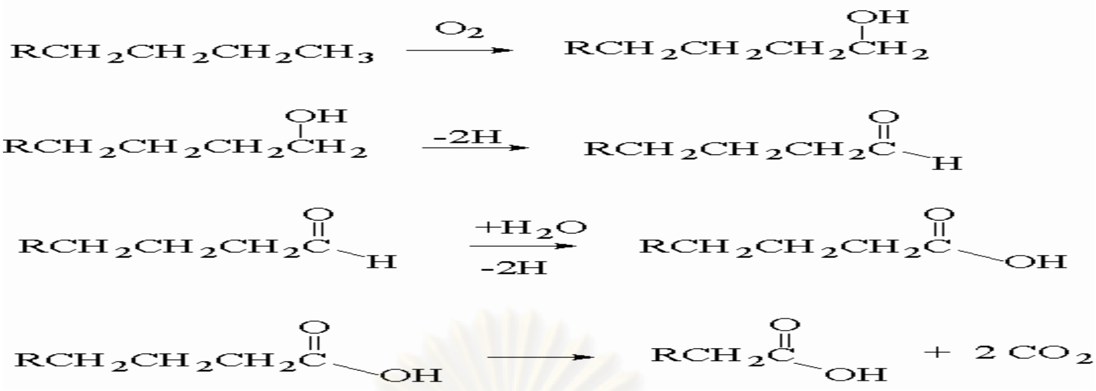


Figure 2.2 Structural formula of carbonyl group, aldehydes , and ketone.

2.7 Degradation Pathways of Straight Chain Hydrocarbon

Although there are many organic chemicals, there are basically two degradation pathways. The common aspect of both degradation pathways is the addition of an -OH function to the molecule. The first step in the breakdown of organic chemicals is to add a hydroxyl group (-OH) to the molecule. The steps that follow the addition of the hydroxyl depend upon whether the molecule is a straight chain hydro carbon or an aromatic molecule (i.e., contains a benzene ring).

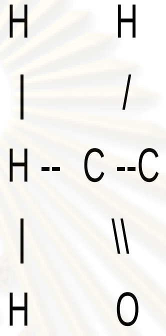


The first step in the degradation of a straight chain hydrocarbon is the formation of a hydroxyl group on a terminal methyl carbon. This can be considered as the "insertion" of an oxygen atom into a carbon-hydrogen bond. This product is called an alcohol (because of the -OH). The second step involves the loss of two hydrogen atoms, forming an aldehyde. The third step involves further oxidation of the terminal carbon, this time taking it from an aldehyde to a carboxylic acid. Once the carboxylic acid is formed, the molecule can undergo b -oxidation. In b -oxidation, the carboxylic acid is reduced in length by two carbon atoms forming a new, shorter straight-chain carboxylic acid and two carbon dioxide molecules.

2.8 Acetaldehyde

Acetaldehyde is a colorless, flammable liquid, volatile at ambient temperature and pressure, with an irritating odor. Acetaldehyde can be used in a wide variety of chemical reactions, many of which are useful in commercial processes. The commercial uses of acetaldehyde include the manufacture of acetic acid, acetic anhydride, pyridines, peracetic acid, penteerthritol, ethyl acetate, alkylamines, lactic acid and crotonaldehyde. Acetaldehyde is also known by a variety of synonyms which include acetic aldehyde, ethanol, ethyl aldehyde and methyl formaldehyde. The molecular formula of Acetaldehyde is CH3CHO.

Acetaldehyde CH_3CHO H_4C_2O



$$\begin{array}{ccccc} H & & & & H \\ | & & & & / \\ H\text{--} & C & \text{--}C & & \\ | & & & \backslash\backslash & \\ H & & & & O \end{array}$$

Acetaldehyde is highly mobile in the environment, and is not naturally removed or detoxified at a rate that would significantly reduce public exposure. The International Agency for Research on Cancer (IARC) classified acetaldehyde as a possible human carcinogen (2B), based on sufficient evidence in animals and inadequate evidence in humans (International Agency for Research on Cancer, 1985). The United States Environmental Protection Agency (U.S. EPA) has decided that acetaldehyde is a "probable human carcinogen" (B2). The OEHHA staff has concluded that at ambient concentrations acetaldehyde may cause or contribute to an increase in mortality or serious illness and may therefore pose a potential hazard to human health.

2.8.1 Production of Acetaldehyde

Acetaldehyde is the product of incomplete combustion emitted from a variety of sources. It can be formed in polluted ambient atmospheres from a variety of such sources as stacks, tailpipe exhaust and fires, as well as formed in the atmosphere as a result of photochemical oxidation of hydrocarbons and free radical reactions involving hydroxyl radicals. In urban areas, emissions are primarily from mobile sources with some contribution from stationary sources. The largest sources statewide of directly emitted acetaldehyde are from combustion of fuels from mobile sources, agricultural burning, and wildfires. Direct sources are estimated to contribute approximately 44 percent of the acetaldehyde in the atmosphere. Photochemical oxidation is estimated to contribute 56 percent of the ambient acetaldehyde as predicted by the Urban Airshed model. Concentrations via photochemical oxidation can vary significantly depending on the season, location, meteorological conditions, and time of day. Mobile and stationary sources emit reactive organic gases such as ethyl peroxide, and ethoxy radicals which are precursors of photochemically generated acetaldehyde. Reductions of these hydrocarbon precursors can be expected to reduce the contribution of acetaldehyde from photochemical oxidation.

2.8.2 Gas Phase Chemistry of Acetaldehyde

Acetaldehyde is formed in the troposphere by the photochemical oxidation of many types of organic compounds, including naturally occurring compounds such as terpenes, as well as mobile and stationary sources such as propene, ethane, propane, ethanol, butenol, hexanol, propionaldehyde, acrolein, phenols, aromatic compounds, ethyl containing compounds and chlorinated organic, (Grosjean D. et al., 1993, 1994).

According to their studies, the atmospheric transformation chemistry of acetaldehyde is similar to formaldehyde. Like formaldehyde, it can be both produced and destroyed by atmospheric chemical formation. The reaction rate of acetaldehyde with OH is the same as formaldehyde. However, there are important differences between these two compounds. Acetaldehyde photolysis, much more slowly than formaldehyde. Formaldehyde produces CO upon reaction or photolysis. Acetaldehyde upon reaction or photolysis, produces organic radicals that ultimately form peroxyacetyl nitrate (PAN) and formaldehyde. The oxidation of acetaldehyde by OH, oxygen atoms, and NO_3 radicals to form a CH_3CO that rapidly reacts with atmospheric O_2 to form peroxyacetyl radical $CH_3C(O)\ OO$. This radical can then react with atmospheric NO and NO_2. The reaction with NO_2 produces peroxyacetyl nitrate (PAN), whereas the reaction with NO ultimately produces formaldehyde. Thus, the major acetaldehyde decomposition products are formaldehyde and PAN both which are toxic compounds. However, in neither case, acetaldehyde is the dominant source of these two compounds.

2.8.3 Health Effects Caused by Acetaldehyde

Exposure to high concentration of acetaldehyde will cause severe eye irritation, corneal injury, and lachrymator (increases the flow of tears), delayed pulmonary edema, and respiratory tract infection. This compound also cause skin irritation, skin sensitization, and an allergic reaction, which becomes evident upon re-exposure to this compound. Inhalation of large amounts may cause respiratory stimulation, followed by respiratory depression, convulsions and possible death due to respiratory paralysis. When swallowed or ingested, acetaldehyde may cause central nervous system depression, gastrointestinal irritation with nausea, dizziness, vomiting and diarrhea. Prolonged or repeated exposure will cause skin dermatitis, erythema and burns, while prolonged or repeated eye contact will cause conjunctivitis. Long term studies of acetaldehyde found that it caused laryngeal cancer in hamsters and nasal cancer in rats.

Table 2.3 Carcinogenicity of acetaldehyde.

ACGIH	Group A3 Confirmed animal carcinogen with unknown relevance to humans.
U.S. E.P.A.	Carcinogen, initial date 4/1/88
NTP	Suspected carcinogen
IARC	Group 2B carcinogen Sufficient studies for animal carcinogen, insufficient data for human

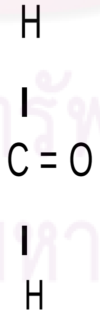
2.9 Formaldehyde

The chemical compound formaldehyde (also known by its IUPAC name methanal, is a gas with a strong pungent smell. It is the simplest aldehyde. Its chemical formula is HCHO, sometimes rendered as H_2CO. It has a boiling point of -21◦C (262 K). Formaldehyde was discovered by the Russian chemist Aleksandr Butlerov in 1859.

Although formaldehyde is a gas at room temperature, it is readily soluble in water, and it is most commonly sold as a 37% solution in water called by trade names such as *formalin* or *formol*. In water, formaldehyde polymerizes, and formalin actually contains very little formaldehyde in the form of HCHO monomer. Usually, these solutions contain a few percent methanol to limit the extent of polymerization.

Formaldehyde exhibits most of the general chemical properties of the aldehydes, except that is generally more reactive than other aldehydes. Formaldehyde is a potent electrophile, and it can participate is electrophilic aromatic substitution reactions with aromatic compounds, and it can undergo electrophilic addition reactions with alkenes. In the presence of basic catalysts, formaldehyde undergoes a Cannizaro reaction to prouduce formic acid and methanol. Formaldehyde is readily oxidized by atmospheric oxygen to form formic acid. Formaldehyde solutions must be kept tightly sealed to prevent this from happening in storage.

Formaldehyde CH_2O HCHO



$$\begin{array}{c} H \\ | \\ C = O \\ | \\ H \end{array}$$

Formaldehyde reversibly polymerizes to produce its cyclic trimer, 1,3,5-trioxane or the linear polymer polyoxymethylene. Formation of these substances makes formaldehyde's gas behavior differ substantially from the ideal gas law, especially at high pressure or low temperature. Production of formaldehyde resins accounts for more than half of formaldehyde consumption. Other formaldehyde derivatives include diphenylmethane diisocyante, an important component in polyurethane paints and foams, and hexamethylene tetramine, which is used in phenol-formaldehyde resins and to make the explosive RDX. Because formaldehyde resins are used in many construction materials, including plywood, carpet, and spray-on insulating foams, and because these resins slowly give off formaldehyde over time, formaldehyde is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air, inhaled formaldehyde can irritate the eyes and mucus membranes, resulting in watery eyes, headache, a burning sensation in the throat, and difficulty breathing.

Large formaldehyde exposures, for example from drinking formaldehyde solutions, are potentially lethal. Formaldehyde is converted to formic acid in the body, leading to a rise in blood acidity, rapid, shallow breathing, hypothermia, and coma or death. People who have ingested formaldehyde require immediate medical attention.

2.9.1 Production of Formaldehyde

Formaldehyde readily results from the incomplete combustion of carbon-containing materials. It may be found in the smoke from forest fires, in automobile exhaust, and in cigarette smoke. In the atmosphere, formaldehyde is produced by the action of sunlight and oxygen on atmospheric methane and other hydrocarbons. Small amounts of formaldehyde are produced as a metabolic byproduct in most organisms, including humans. Although formaldehyde is a gas at room temperature, it is readily soluble in water, and it is most commonly sold as a 37% solution in water called by trade names such as *formalin* or *formol*. In water, formaldehyde polymerizes, and formalin actually contains very little formaldehyde in the form of HCHO monomer. Usually, these solutions contain a few percent methanol to limit the extent of polymerization. Formaldehyde exhibits most of the general chemical properties of the aldehydes, except that is generally more reactive than other aldehydes. Formaldehyde is a potent electrophile, and it can participate is electrophilic aromatic substitution reactions with aromatic compounds, and it can undergo electrophilic addition reactions with alkenes. In the presence of basic catalysts, formaldehyde undergoes a Cannizaro reaction to prouduce formic acid and methanol.

Industrially, formaldehyde is produced by the catalytic oxidation of methanol. The most commonly catalysts are silver metal, and a mixture of an iron oxide with molybdenum. In the more commonly used iron oxide system, methanol and oxygen react at 400◦C to produce formaldehyde according to the chemical equation

$$CH_3OH + \tfrac{1}{2}\,O_2 \longrightarrow HCHO + H_2O$$

The silver-based catalyst is usually operated at a higher temperature, about 650◦C. On it, two chemical reactions simultaneously produce formaldehyde: the one shown above, and the dehydrogenation reaction

$$CH_3OH \longrightarrow HCHO + H_2$$

2.9.2 Uses of Formaldehyde

Formaldehyde kills most bacteria, and so a solution of formaldehyde in water is commonly used as a disinfectant or to preserve biological specimens. It is also used as a preservative in vaccinations. . A chemical used as a preservative and in bonding agents. It is found in household products such as plywood, furniture, carpets, and some types of foam insulation. It is also a by-product of combustion and is a strong-smelling, colorless gas that is an eye irritant and can cause sneezing, coughing, and other health problems. Most formaldehyde, is used in the production of polymers and other chemicals. When combined with phenol, urea, or melamine, formaldehyde produces a hard thermoset resin. These resins are commonly used in permanent adhesives, such as those used in plywood or carpeting. They are also foamed to make insulation, or cast into molded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption. Formaldehyde is also used to make numerous other chemicals. Many of these are polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include diphenylmethane diisocyante, an important component in polyurethane paints and foams, and hexamethylene tetramine, which is used in phenol-formaldehyde resins and to make the explosive RDX.

2.9.3 Health Effects Caused by Formaldehyde

Because formaldehyde resins are used in many construction materials, including plywood, carpet, and spray-on insulating foams, and because these resins slowly give off formaldehyde over time, formaldehyde is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air, inhaled formaldehyde can irritate the eyes and mucus membranes, resulting in watery eyes, headache, a burning sensation in the throat, and difficulty breathing. Large formaldehyde exposures, for example from drinking formaldehyde solutions, are potentially lethal. Formaldehyde is converted to formic acid in the body, leading to a rise in blood acidity, rapid, shallow breathing, hypothermia, and coma or death. People who have ingested formaldehyde require immediate medical attention.

In the body, formaldehyde can cause proteins to irreversibly bind to DNA. Laboratory animals exposed to large doses of inhaled formaldehyde over their lifetimes have developed more cancers of the nose and throat than are usual, as have workers in particle-board mills. However, some studies suggest that smaller concentrations of formaldehyde like those encountered in most buildings have no carcinogenic effects. IARC classified Formaldehyde human carcinogen (International Agency for Research on Cancer, 2004).

Table 2.4 Carcinogenicity of formaldehyde.

ACGIH	Group A1 Studies show sufficient evidence of carcinogenicity to human
U.S. E.P.A.	Group A1 Studies show sufficient evidence of carcinogenicity to human
IARC	Group A1 Studies show sufficient evidence of carcinogenicity to human

2.9.4 Uptake, Metabolism, and Excretion of Formaldehyde

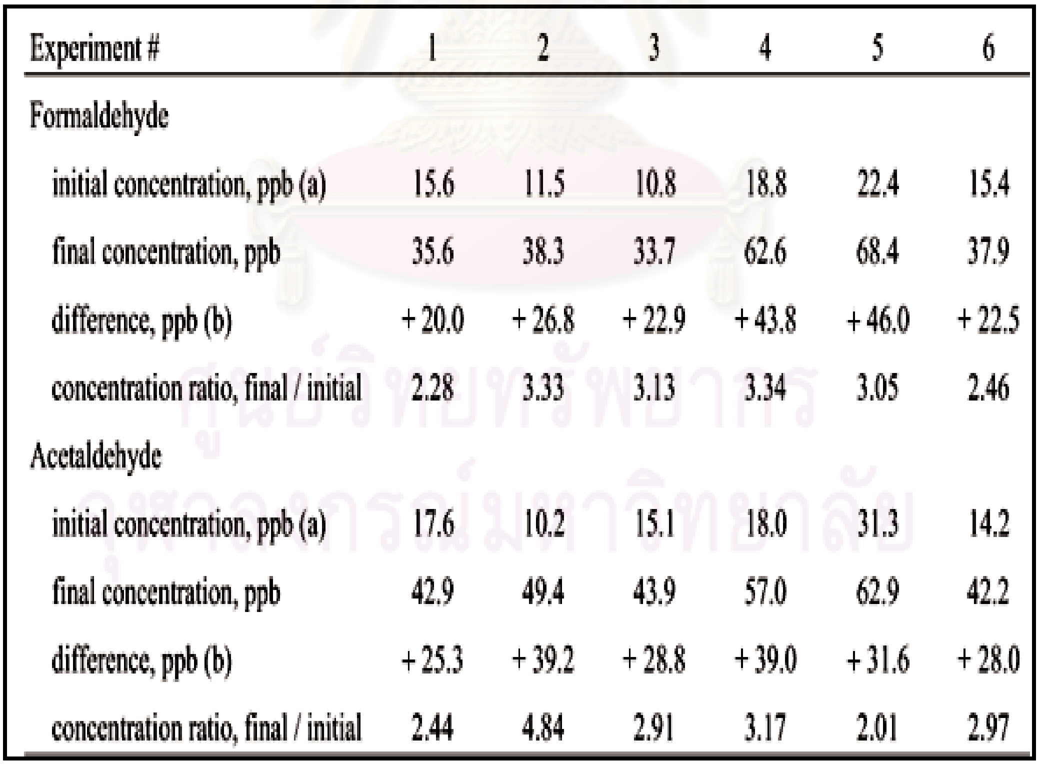
Formaldehyde is readily absorbed via the respiratory and gastrointestinal routes. Dermal absorption of formaldehyde appears to be very slight. Increases in blood concentrations of formaldehyde were not detected in rats or human beings exposed to formaldehyde through inhalation, because of rapid metabolism. Absorbed formaldehyde is metabolized rapidly to formate, or enters the one-carbon pool to be incorporated into other molecules. There are two pathways of final elimination, namely, in exhaled air or via the kidneys.

2.10 Formation of Ozone in Urban Air by Photochemical Oxidation of Hydrocarbons: Captive Air Experiments in Porto Alegre, RS

Captive air experiments have been carried out at a downtown location in Porto Alegre, RS, where both methyl-tert-butyl ether (MTBE) and ethanol are being used as oxygenated fuels. In their captive air experiment, ambient air was introduced in a Teflon chamber and exposed to sunlight for several hours, thus allowing photochemical reactions to take place under "real-world" conditions. Parameters measured in six experiments, the first of their kind to be carried out in Brazil, included oxides of nitrogen (NO and NO_2), carbon monoxide, carbon dioxide, methane, non-methane hydrocarbons, formaldehyde, acetaldehyde, ethanol, MTBE, and the photochemical oxidants ozone and peroxyacetyl nitrate(PAN) (Grosjean, E. et al., 1999).

Photochemical conversion of NO to NO_2 and photochemical production of ozone (maximum concentrations 156-348 ppb) and PAN (maximum 13.3-29.5 ppb) were observed in all experiments, together with net (formation minus removal) photochemical production of formaldehyde and acetaldehyde. For each experiment, the contributions of each pollutant to reaction with the hydroxyl radical (OH) and to the production of ozone have been calculated. The results indicated that on the average, 10 compounds were the most important with respect to the production of ozone (listed in order of decreasing importance): ethylene, carbon monoxide, acetaldehyde, (m + p)-xylene, formaldehyde, propene, 1,2,4-trimethylbenzene, toluene, ethanol and trans-2-pentene (Grosjean E. et al., 1999). MTBE makes only a small contribution to reaction with OH (ranked #27) and to the production of ozone (ranked #30), and plays only a minor photochemical role in the atmosphere of Porto Alegre.

Table 2.5 Net production of formaldehyde and acetaldehyde in Porto Alegre captive air experiments.



Experiment #	1	2	3	4	5	6
Formaldehyde						
initial concentration, ppb (a)	15.6	11.5	10.8	18.8	22.4	15.4
final concentration, ppb	35.6	38.3	33.7	62.6	68.4	37.9
difference, ppb (b)	+ 20.0	+ 26.8	+ 22.9	+ 43.8	+ 46.0	+ 22.5
concentration ratio, final / initial	2.28	3.33	3.13	3.34	3.05	2.46
Acetaldehyde						
initial concentration, ppb (a)	17.6	10.2	15.1	18.0	31.3	14.2
final concentration, ppb	42.9	49.4	43.9	57.0	62.9	42.2
difference, ppb (b)	+ 25.3	+ 39.2	+ 28.8	+ 39.0	+ 31.6	+ 28.0
concentration ratio, final / initial	2.44	4.84	2.91	3.17	2.01	2.97

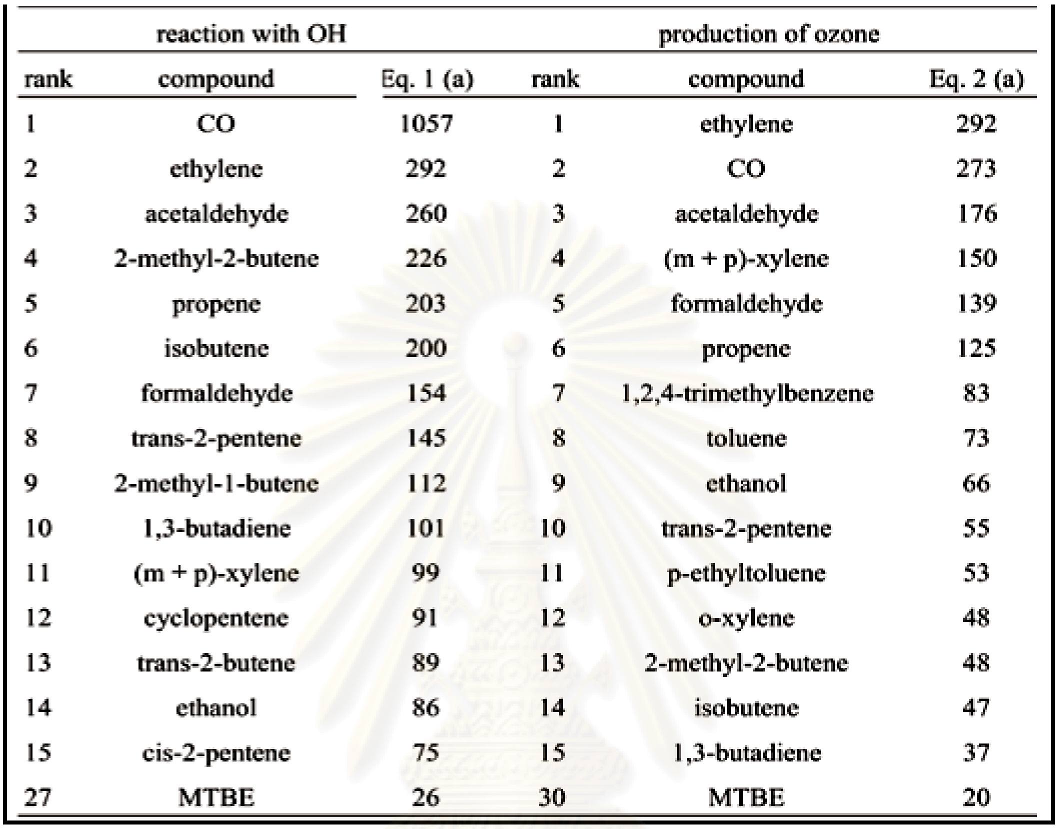
In their captive air experiment, formaldehyde and acetaldehyde initially present were rapidly removed by photolysis and by reaction with the hydroxyl radical (OH). At the same time, the two aldehydes were formed as oxidation products of many of the VOC initially present. In turn, a fraction of the aldehydes thus formed were removed by photolysis and by reaction with OH. This competition between photochemical formation and photochemical removal may result in a net production or a net loss of formaldehyde and acetaldehyde. Net production of formaldehyde ranged from 20 to 46 ppb, net production of acetaldehyde ranged from 25 to 39 ppb, and concentration ratios (final / initial) were *ca*. 2.3-3.3 for formaldehyde and *ca.* 2.0-4.8 for acetaldehyde. The data given were likely to be lower limits for actual net production of aldehydes, because of two reasons. First, measured final concentrations may be lower than actual values if loss of aldehydes to the chamber wall becomes important late in the experiment (Grosjean, D.1985, Grosjean, E. et al.,1996). This is because the volume of the Teflon chamber decreases and the chamber surface-to-volume (S/V) ratio correspondingly increases as air is withdrawn from the chamber for the purpose of measuring NO_x, ozone and PAN: this increase in S/V may lead to an increase in the rate of loss of aldehydes to the chamber walls. Second, the samples collected when levels of ozone are high may suffer from a negative bias due to reaction of ozone with the DNPH derivatives of formaldehyde and acetaldehyde during sampling, and thus measured values may be lower limits for actual concentrations.

It is of interest to examine the relative contribution of the VOC to photochemical formation of ozone in the captive air experiments. This can be done by ranking the VOC according to their ability to react with the hydroxyl radical (all VOC react with OH, leading to photochemically reactive products including free radicals). VOC can also be ranked with respect to their ability to produce ozone. To rank VOC with respect to reaction with OH, they calculated the product of the VOC concentration and of the VOC-

OH reaction rate constant. The result of their experiment showed that, with respect to production of ozone, ethylene ranked #1, followed closely by carbon monoxide, followed by, in order of decreasing importance, acetaldehyde, (m + p)-xylene, formaldehyde, propene, 1,2,4-trimethylbenzene, toluene, ethanol, trans-2-pentene, p-ethyltoluene, o-xylene, 2-methyl-2-butene, isobutene and 1,3-butadiene. MTBE is ranked #30 and its contribution to ozone production is small, *e.g. ca*. 9 times less than that of acetaldehyde and *ca*. 3 times less than that of ethanol. The data in Table 2.5 indicate that CO, ethylene and acetaldehyde are the three most important contributors to both reaction with OH and production of ozone.

Ethanol fuel plays a significant role, due to emissions of unburned ethanol (ranked #9 for ozone production and #14 for reaction with OH) and also due to acetaldehyde emissions from ethanol-fueled vehicles (acetaldehyde ranks #3 for ozone production and #3 for reaction with OH). To rank VOC with respect to ozone formation, they calculated the product of the VOC concentration and the VOC maximum incremental reactivity coefficient (MIR= grams of ozone formed per gram of VOC). Table 2.5 shows the Ranking of top 15 pollutants with respect to OH and ozone

Table 2.6 Ranking of “top 15 pollutants with respect to OH and ozone production, (average of 6 captive air experiments).



reaction with OH			production of ozone		
rank	compound	Eq. 1 (a)	rank	compound	Eq. 2 (a)
1	CO	1057	1	ethylene	292
2	ethylene	292	2	CO	273
3	acetaldehyde	260	3	acetaldehyde	176
4	2-methyl-2-butene	226	4	(m + p)-xylene	150
5	propene	203	5	formaldehyde	139
6	isobutene	200	6	propene	125
7	formaldehyde	154	7	1,2,4-trimethylbenzene	83
8	trans-2-pentene	145	8	toluene	73
9	2-methyl-1-butene	112	9	ethanol	66
10	1,3-butadiene	101	10	trans-2-pentene	55
11	(m + p)-xylene	99	11	p-ethyltoluene	53
12	cyclopentene	91	12	o-xylene	48
13	trans-2-butene	89	13	2-methyl-2-butene	48
14	ethanol	86	14	isobutene	47
15	cis-2-pentene	75	15	1,3-butadiene	37
27	MTBE	26	30	MTBE	20

2.11 Acetaldehyde Concentration in California Air.

Total direct outdoor acetaldehyde emissions from mobile, stationary and area sources as based on ARB's 1987 emission inventory in California which were estimated to be approximately 11,000-24,000 tons per year. Mobile sources, which include on-road motor vehicles and other transportation sources such as trains, ships, farm and utility equipment, emitted approximately 3,7OO to 7,800 tons of acetaldehyde or 15 to 32 percent of direct emissions (Grosjean, E. et al.,1996b). Stationary point sources such as fuel combustion sources, refineries and coffee bean roasters emitted approximately 820 to 1,000 tons (3 to 4 percent) of acetaldehyde. Stationary area sources include wildfires, agricultural burning and management burning, and diesel combustion in internal combustion engines at oil and gas fields, etc. The staff estimates that these stationary area sources emitted approximately 7,000 to 15,000 tons (29 to 62 percent) of acetaldehyde.

Gasoline containing the oxygenate additives ethanol or ethyl tertiary-butyl ether (ETBE), upon combustion, may result in increased acetaldehyde emissions. However, it is not known to what extent ethanol or ETBE will be used as a winter oxygenate in California fuels and, therefore, the resulting effect on acetaldehyde emissions. The overall effect of the vehicular emission standards and the gasoline specifications on acetaldehyde concentrations is a complex issue. Future acetaldehyde emissions will depend on the turnover rate of older vehicles to LEVs, the primary acetaldehyde contributions from oxygenated additives, such as ethanol and ethyl tertiary-butyl ether, the decrease of ROG from the combustion of Phase 2 reformulated gasoline, and possible use of ethanol.

Acetaldehyde is routinely monitored by the statewide ARB tonics monitoring network. Basin-specific mean annual concentrations vary from a minimum of 2.93 micrograms per cubic meter in the South Central Coast Air Basin to a maximum of 5.06 micrograms per cubic meter in the South Coast Air Basin (based on 24hour sample averages). The overall estimated mean statewide exposure, weighted by population, is estimated to be 4.19 micrograms per cubic meter. The population-weighted exposure is based on 20 million people represented by the tonics monitoring network (out of the 30 million total California populations).

Studies conducted in the South Coast Air Basin since 1980 have reported data for short-term (30 minute to 2 hour sample averages) ambient outdoor concentrations vary from 1.8 microgram per cubic meter) to 70.2 micrograms per cubic meter, with the most recent concentrations measured during the South Coast Air Quality Study (SCADS)

(1987) with a range of 1.6 to 44.1 micrograms per cubic meter in one hour samples (Grosjean, E. et al. 1997). The SCADS was an integrated air quality study whose overall goal was to develop a comprehensive and properly archived air quality and meteorological data base for the South Coast Air Basin which can be used to test, evaluate, and improve elements of air quality simulation models for oxidants, NO2, PMl0, fine particles, visibility, toxic air contaminants, and acid species. Reports of ambient air sampling of two rural regions, Point Barrow, Alaska and Whiteface Mountain, New York provide examples of 'background' concentrations of 1.4 micrograms per cubic meter of acetaldehyde.

2.12 Transportation Related Air Toxics

In 2001, EPA issued its first Mobile Source Air Toxics Rule which identified 21 Mobile Source Air Toxic compounds or MSATS as being hazardous air pollutants that required regulation. Among these compounds , five compounds were identified as having the greatest influence on health that included: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein, (Air Toxics-Air Quality-FHWA). These five pollutants are referred to as priority MSAT. More recently, EPA issued a second MSAT Rule in February 2007 which generally supported the findings in the first rule and provided additional recommendations of compounds having the greatest impact on health. The rule also identified several engine emission certification standards that must be implemented. Unlike the criteria pollutants, toxics do not have National Ambient Air Quality Standards (NAAQS) associated with them which makes evaluation of their impacts more subjective. Their ongoing work in air toxics includes a research program to determine and quantify the contribution of mobile sources to air toxic emissions, the establishment of policies for addressing air toxics in environmental reports, and the assessment of scientific literature on health impacts associated with motor vehicle toxic emissions. among the gaseous hydrocarbon components of Diesel Exhaust Organic Gases (DEOG) individually known to be of toxicologic relevance are the aldehydes (e.g., formaldehyde, acetaldehyde, acrolein), benzene, 1,3-butadiene, and Polycyclic Organic Matter (POM). A number of toxicologically relevant organic compounds are on the Diesel Particulate Matter (DPM). The organics, in general, range from about 20% to 40% of the particle weight, though higher and lower percentages are also reported. The EPA's findings are similar to findings from other agencies. For example, the California Air Resources Board (CARB) has identified 10 air toxics of concern, five of which are emitted by on-road mobile sources: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and diesel PM (California Air Resources Board, 2007). There is overlap among the substances listed in Table 2-7. For example, POM includes a wide range of substances, including polycyclic aromatic hydrocarbons (PAHs) and sometimes the dioxins and furans; the diesel emissions categories include several of the individual MSAT as well. EPA's Health Assessment Document for Diesel Exhaust stated that compounds present on the particle and in the gases are individually known to have mutagenic and carcinogenic properties. For example, PAHs, nitro-PAHs, and oxidized PAH derivatives are present and comprise about 1% or less of the DPM mass. (U.S. Environmental Protection Agency, 2002).

In summary, the highest-risk air toxics from on-road vehicles have been identified by the EPA and others as DPM/DEOG, are: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein.

Table 2.7 EPA's 21 Mobile Source Air Toxics and (Five priority MSAT)

Specific Organic Compounds	Compounds Containing Inorganics	Pollutant Categories
Acetaldehyde Formaldehyde Acrolein Benzene 1,3-Butadiene Ethylbenzene n-Hexane Methyl tert-Butyl Ether (MTBE) Naphthalene Styrene Toluene Xylene	Arsenic Compounds Chromium Compounds Lead Compounds Mercury Compounds Manganese Compounds Nickel Compounds	Diesel Particulate Matter (DPM) + Diesel Exhaust Organic Gases (DEOG) Polycyclic Organic Matter (POM) Polycyclic Chlorinated Di-benzop-dioxins PCDDs) and Polycyclic Chlorinated Dibenzo-p-furans (PCDFs) ("Dioxins/Furans")[a]

2.13 Quantification of Cancer Risks from Air Toxics

Although there are health risks from air toxics aside from cancer risks, health-related conclusions regarding air toxics are often quantified only in terms of cancer risk. Cancer is one of the leading causes of mortality in the United States: approximately one in every four deaths is from cancer, and approximately 40% of people in the United States will develop an invasive cancer sometime during their lifetime (American Cancer Society, 2002). With respect to air pollution (and many other forms of environmental pollution), associated cancer risks are often measured in terms of "excess deaths" due to the environmental exposure, usually per million people. For example, a lifetime risk of 10^{-5} corresponds to 10 excess deaths per million people; a lifetime risk of 10^{-4} corresponds to 100 excess deaths per million people. The EPA's risk management policy for stationary sources, as identified in its 1999 Residual Risk Report to Congress (based upon the EPA's 1989 rulemaking for benzene emissions standards), is to "[strive] to provide maximum feasible protection against risks to health from hazardous air pollutants by: (1) protecting the greatest number of persons possible to an individual lifetime risk level no higher than approximately 1 in 1 million and, (2) limiting to no higher than approximately 1 in 10 thousand the estimated risk that a person living near a plant would have. (Loh, M. et al., 2007), has stated that estimated excess cancer risks for background air pollution even in remote areas of the United States are on the order of 10^{-5}. As mentioned previously, the MATES-II study calculated an excess cancer risk of 1,400 per million people, 90% of which was attributed to mobile sources. A common means of assessing cancer risk is to multiply the concentration of each carcinogenic substance by a Unit Risk Factor (URF) for that substance. The risks for each substance are then added to arrive at a total risk. As an example of the extent to which there are differences in opinions regarding the "correct" value for URFs.

Table 2.8 Unit risk values of Acetaldehyde and formaldehyde given by OEHHA and U.S. E.P.A.

Pollutant	OEHHA[a]	U.S. EPA[b]	Difference between OEHHA and U.S. EPA
Acetaldehyde	2.7×10^{-6}	2.2×10^{-6}	20%
Formaldehyde	6.0×10^{-6}	1.3×10^{-5}	factor of approx. 2

[a] Data are from California Office of Environmental Health Hazard Assessment, http://www.oehha.ca.gov/risk.html, as of November 18, 2002.

[b] Unless noted otherwise, data are from EPA Integrated Risk Information

It should be noted that the differences presented in Table 2.8, are not necessarily representative of the uncertainties in these values, or the cancer risks derived from them. OEHHA and EPA often reference the same studies when evaluating cancer risks, and therefore the differences are a reflection only of the differences in opinion regarding which URFs should be used. Uncertainties associated with the accuracy of the risk calculations are actually higher, as they depend upon not only these differences of opinion, but also any uncertainties associated with the data used to develop the URF, or the URF approach in general.

After reviewing available studies on formaldehyde carcinogenicity, the OEHHA staff estimates that the best value for the 95 percent upper confidence limit of cancer risk to be 7×10^{-6} ppb^{-1} [$6 \times 10^{-6} (\mu g/m^3)^{-1}$]. This corresponds to up to 7 potential excess cancers among a million people continuously exposed to 1 ppbv formaldehyde over a 70-year lifetime. The staff of the OEHHA recommends that the unit risk for acetaldehyde is 4.8 x 10^{-6} per part per billion (2.7 x 10^{-6} per microgram per cubic meter) be considered the "best value of the upper bound of risk." This is similar to the value calculated by the U.S. EPA to 2.2 x 10^{-6} per microgram per cubic meter. This value is based on data from a recent bioassay in male rats. This unit risk, coupled with a lifetime exposure to one part per billion, would yield 4.8 excess potential cancer cases per million people. The use of this "best value" with California's average ambient acetaldehyde exposure concentration of two parts per billion volume (3.6 microgram per cubic meter) yields 9.6 excess potential cancer cases per million people exposed throughout their lives. It can be estimated that up to 288 acetaldehyde-induced potential cancer cases would occur statewide among a population of 30 million people exposed to current ambient concentrations throughout their lives. The upper limit estimate of the number of potential excess cancers due to outdoor airborne acetaldehyde exposure ranges from 2 to 54 per million people exposed throughout their lives, based on California's present average ambient acetaldehyde exposure concentration of 2 parts per billion volume (4 microgram per cubic meter), and an excess cancer risk range of 0.97 x 10^{-6} to 27.0 x 10^{-6} per part per billion (0.54 x 10^{-6} to 15 x 10^{-6} per microgram per cubic meter). This range of risk is based on data from studies in male and female rats. Table 2-2 illustrates differences between URFs assigned by the U.S. EPA, and those assigned by the California Office of Environmental Health Hazard Assessment (OEHHA).

2.14 Ethanol Fuel in Brazil

Brazil is the world’s second largest producer of ethanol and the world’s largest exporter, and it is considered as the world’s first sustainable biofuel economy and the biofuel industry leader. Together, Brazil and the United States lead the industrial world in global ethanol production, accounting together for 70% of the world's production and nearly 90% of ethanol used for fuel. In 2006, Brazil produced 16.3 billion liters (4.3 billion U.S. liquid gallons), which represents 33.3% of the world's total ethanol production and 42% of the world's ethanol used as fuel. Total production is predicted to reach at least 26.4 billion liters (6.97 billion U.S. liquid gallons) for 2008 (Plummer, R., 2006). Brazil's 30 years old ethanol program uses modern equipment and cheap sugar cane as feedstock, the residual cane-waste (bagasse) is used to process heat and power, which results in a very competitive price and also in a high energy balance (output energy/input energy), which varies from 8.3 for average conditions to 10.2 for best practice production. The Brazilian ethanol program provided nearly one million jobs in 2007, and cut 1975–2002 oil imports by a cumulative undiscounted total of US$50 billion. The production of ethanol is concentrated in the Central and Southeast regions of the country, which includes the main producer, São Paulo State. These two regions were responsible for almost 90% of Brazil's ethanol production in 2004 (

There are no longer light vehicles in Brazil running on pure gasoline. Since 1976 the government made it mandatory to blend anhydrous ethanol with gasoline (E20), fluctuating between 10% to 22% and requiring just a minor adjustment on regular gasoline motors. In 1993 the mandatory blend was fixed by law at 22% anhydrous ethanol (E22) by volume in the entire country. By the end of 2006, there were 33,000 filling stations throughout the country with at least one ethanol pump (Plummer, R., 2006). The Brazilian car manufacturing industry developed flexible-fuel vehicles (FFV) that can run on any proportion of gasoline (E20-E25 blend) and hydrous ethanol (E100). Introduced in the market in 2003, the flex-fuel vehicles became a commercial success.

On August 2008, the fleet of "flex" cars and light commercial vehicles had reached 6.2 million new vehicles sold, which represents around 23% of Brazil's light-duty motor vehicle fleet. The success of "flex" vehicles, as they are popularly known, together with the mandatory use of E25 blend of gasoline throughout the country, have allowed ethanol fuel consumption to achieve a 50% market share of the gasoline-powered fleet by February 2008.

2.15 Effects of using Oxygenated Fuels on Formaldehyde and Acetaldehyde Concentration in Denver.

The Denver metropolitan area is the first region in the United States to implement the use of oxygenated gasoline in an effort to reduce ambient CO (Anderson *et al.*, 1994). The program has been mandated since the beginning of 1988 when the majority of the fuel sold contained 8% MTBE with the rest being a 10 vol% ethanol blend. Since then, the additive used has gradually shifted from largely MTBE to largely ethanol. In Colorado, the minimum fleet average oxygen content in the fuel sold is 3.1% by weight oxygen content(Anderson, L.G., 1997). This is to be achieved with at least 50% of the market share being ethanol blended fuels at 3.7% oxygen by weight. The ethanol blended market share is running over 90% in recent years. If one assumes that all of the fuel used is the 3.7% by weight oxygen content ethanol blended fuel, the emissions should change by about a 13% decrease for CO, a 5% increase for NO_x, an 11% decrease for benzene, a 6% decrease for 1,3-butadiene, a 19% increase for formaldehyde, and a 160% increase for acetaldehyde.

Larry G. Anderson and his group from the Department of Chemistry and Center at Denver Environmental Sciences, Denver, has utilized ambient air carbon monoxide concentration data assess the effectiveness of the oxygenated fuels for the reduction of carbon monoxide emissions from vehicles operating in their area. In the Denver metropolitan area about 80% of the CO emissions are believed to come from motor vehicles. Based on his analysis, suggest that there is a 6-10% reduction in the atmospheric concentration of CO in Denver Metropolitan area that could be contributed by the use of oxygenated fuels. His study further suggest that this benefit is only 1-2% at the downtown monitoring site where CO is often at its highest concentrations. He conducted his study for 3 years and observed that there was a reduction in CO ambient concentrations for three years due to the use of oxygenated fuels. The hydrocarbon emission data showed no effect from the use of oxygenated fuels. However, NOx emission data showed 13-16% increase with the use of oxygenated fuels especially in Colorado during the winter, which may have a significant impact on the secondary particulate nitrate contribution to Denver's *brown cloud*. If NO_x emissions increase this much with the use of oxygenated fuels, there might be adverse effects on ozone concentrations related to the use of these fuels. Similar effects on NO_x emissions might occur in areas that are required to use reformulated fuels during summer ozone periods as a means of reducing ozone formation. If NO_x emissions increase for these fuels by nearly 14%, an ozone increase might occur due to the use of these fuels.

2.16 Ambient Carbonyl Compounds in China.

Ambient levels of carbonyl compounds and their possible sources, vehicular exhaust and cooking exhaust, were studied at seven places in Guangzhou, including five districts (a residential area, an industrial area, a botanical garden, a downtown area and a semi-rural area), a bus station and a restaurant during the period of June-September 2003. Nineteen carbonyl compounds were identified in the ambient air, of which acetone was the most abundant carbonyl, followed by formaldehyde and acetaldehyde. Only little changes were found in carbonyl concentration levels in the five different districts because of their dispersion and mixture in the atmosphere in summer. The lower correlations between the carbonyls' concentrations might result from the mixture of carbonyls derived from different sources, including strong photochemical reactions at noon in summer. Formaldehyde and acetaldehyde were the main carbonyls in bus station, while straight-chain carbonyls were comparatively abundant in cooking exhaust. Besides vehicular exhaust, cooking might be another major source of carbonyl compounds in Guangzhou City, especially for high atmospheric environment (Zhang, J. et al., 1999, Feng, Y. et al., 2005).

2.17 Atmospheric levels of formaldehyde and acetaldehyde and their relationship with the vehicular fleet composition in Salvador, Bahia, Brazil

The transportation sector in Brazil accounts for about 21% of the total energy consumption. Despite the great effort to reduce the dependence on foreign oil, 85% of energy is based on petroleum resources, 50% of which is imported. Concerns about air quality and economic impacts have prompted policies to encourage the use of alternative fueled vehicles. Brazilian market: dedicated vehicles operating exclusively on natural gas, and dual-fueled vehicles which can use gasohol and natural gas, gas and alcohol or natural gas and diesel. The fuel is mainly used by taxis, vans and small buses. The total number of vehicles in the city of Rio de Janeiro is 1,810,764 for the year of 2004, distributed in 15% fueled by ethanol, 76% by gasohol, 4% by diesel and 5% by CNG (de Andrade, M.V. et al., 1998).

In the past decade a substantial amount of information on surface atmospheric levels of formaldehyde and acetaldehyde has been generated. However, most of the knowledge about formaldehyde and, principally, of acetaldehyde in the atmosphere comes from measurements in countries where the vehicular fleet is fueled with gasoline and diesel. In this way, information of aldehyde levels, emitted in countries, as is the case in Brazil, where ethanol is used as a fuel and also added to gasoline, as an octane booster (gasohol, gasoline with 18% to 22% v/v ethyl alcohol) are needed.

Data taken at both Rio de Janeiro and Albuquerque (Tanner, et al. 1988), indicated that the larger peroxyaeyl nitrate, peroxyproprionyl nitrate (PPN), is apparently produced in higher levels when ethanol or methyl-t-butyl ether used as oxygenates. PPN has been found to be more toxic than PAN. It is a storage medium for NO2 and will lead to the formation of PAN, peroxides, and aldehydes upon thermal decomposition, i.e., asian air mass is transported downwind. Peroxides produced from these aldehyde emissions can cause increased oxidation of sulfur dioxide to sulfate resulting in decreased visibility and increased acidic deposition. Regional ozone levels may also be affected by changes in these emissions downwind of the urban center.

2.18 Air Pollution in São Paulo and Santiago de Chile: Sources and Impacts

Urban air pollution is a serious issue for millions in Latin America. São Paulo, Santiago de Chile, México City and many other large urban conglomerates. Fast industrialization, large population growth, emissions from the transportation sectors and many other issues are the cause for the air pollution in these mega cities. São Paulo, with 17 million people, 5.5 million vehicles and strong industry suffers from severe particulate matter and ozone exposure. Santiago de Chile with very unfavorable dispersion characteristics also has problems with PM10 and ozone. Health effects in these areas are a public health concern. In Sao Paulo alone, about 30,000 excess deaths are attributable to air pollution issues. There are also critical institutional issues in the São Paulo metropolitan area, which has 39 municipalities, as well as three other metropolitan areas within a 100-km radius. In Santiago de Chile, a dry climate makes resuspended soil dust an important PM10 component, and vehicle emissions produces high concentration of secondary organic aerosols. Old diesel buses make black carbon concentrations very high in Santiago. An extensive aerosol source apportionment studies for several years, using PIXE as trace element analysis technique and multivariate statistical analysis to separate and quantify aerosol sources in Santiago and Sao Paulo was done. Results from 5 years studies in both Santiago and Sao Paulo indicated that vehicles and soil dust dominates the picture, with a strong sulfate component in Santiago de Chile.

2.19 Measurement of Air Toxics in Thailand

Due to increase in prices of fossil fuel the government of Thailand introduced a policy to use alternative fuels. In the beginning of 2004 the use of gasohol has been slowly increasing, until 2007 the sale of gasohol significantly increased. At present, gasohol is widely used especially for cars and motorcycles.

The Pollution Control Department (PCD) conducted a project to measure Air Toxics in Bangkok during 2006 to 2008 which focused on: (1) BTEX compounds such as benzene, toluene, ethylbenzene, xylene, and 13 butadiene; (2) carbonyl compounds such as formaldehyde, acetaldehyde, acrolein acetone and propionaldehyde. The objective of their project was to monitor the emission of air pollutants from cars and motorcycles that use gasohol as fuel. They conducted their measurements directly in the exhaust pipes of the cars and motorcycles studied. In addition PCD also conducted a measurement of toxic air pollutants in ambient air at 3 sites in Bangkok by collecting air samples using DNPH active samplers every 6 days for a period of 12 months during 2006. From their studies, it was found that the emission of toxic air pollutants from cars using gasohol compared to gasoline fuelled cars indicated that carbon monoxide, benzene and 1,3 butadiene had decreased, 14.97%, 12.86% and 55.71% respectively as seen in Table 2.9 . Hydrocarbons, NOx, carbon dioxide, ethylbenzene, xylene, toluene, formaldehyde, and acetaldehyde increased to 5.73%, 12.20%, 3.93%, 122.34%, 177.07%, 6.20%, 20.72%, and 127.275 respectively as seen in Table 2.10. The result of their tests also indicated that the emission of toxic air pollutants from motorcycles using gasohol compared to gasoline fuelled motorcycles that hydrocarbons, carbon monoxide, 1,3 butadiene, ethylbenzene, formaldehyde and acetaldehyde decreased, 5.56%, 10.52%, 15.52%, 30.69%, 34.20%, and 2.59% respectively. The concentration of benzene, NOx, carbon dioxide, xylene and toluene increased to 21.78%, 17.39%, 5.56%, 587.90% and 21.19% respectively. The result of their study emphasize that concentration level of hydrocarbon and carbon monoxide decreased in motorcycles using gasohol as seen in Table 2.11while the concentration of formaldehyde and acetaldehyde also decreased in motorcycles using gasohol as seen in Table 2.12. It also further indicated that motorcycles are suitable to use gasoline because it emits lesser concentration of toxic air pollutants as see in Table 2.13.

Table 2.9 Emission of conventional air pollutants from cars using gasohol

Air Toxic Pollutants	Emission changes from cars using gasohol compared to gasoline
Hydrocarbon	5.73%
Carbon Monoxide (CO)	-14.97%
Oxide of Nitrogen (NOx)	12.20%
Carbon Dioxide (CO2)	3.93%

Source: Measurement of Toxic air Pollutants from gasohol fuelled cars. Executive Summary, Pollution Control Department, April 2008.

Table 2.10 Emission of toxic air pollutants from cars using gasohol in Thailand

Air Toxic Pollutants	Emission changes from cars using gasohol compared to gasoline
Benzene	-12.86%
1,3 Butadiene	-55.71%
Ethylbenzene	122.34%
Xylene	177.07%
Toluene	6.20%
Formaldehyde	20.72%
Acetaldehyde	127.27%

Source: Measurement of Toxic air Pollutants from gasohol fuelled cars. Executive Summary, Pollution Control Department, April 2008

Table 2.11 Emission of conventional air pollutants from motorcycles using gasohol

Air Toxic Pollutants	Emission changes from motorcycles using gasohol compared to gasoline
Hydrocarbon	-5.56%
Carbon Monoxide (CO)	-10.52%
Oxide of Nitrogen (NOx)	17.39%
Carbon Dioxide (CO2)	5.56%

Source: Measurement of Toxic air Pollutants from gasohol fuelled cars. Executive Summary, Pollution Control Department, April 2008.

Table 2.12 Emission of toxic air pollutants from motorcycles using gasohol in Thailand

Air Toxic Pollutants	Emission changes from motorcycles using gasohol compared to gasoline
Benzene	21.78%
1,3 Butadiene	-15.52%
Ethylbenzene	-30.69%
Xylene	587.90%
Toluene	21.19%
Formaldehyde	-34.20%
Acetaldehyde	-2.59%

Source: Measurement of Toxic air Pollutants from gasohol fuelled cars. Executive Summary, Pollution Control Department, April 2008

Table 2.13 Emission of toxic air pollutants from motorcycles using gasoline in Thailand

Air Toxic Pollutants	Emission changes from motorcycles using gasoline
Benzene	-29.35%
1,3 Butadiene	-2.35%
Ethylbenzene	-18.71%
Xylene	11.16%
Toluene	-24.75%
Formaldehyde	12.90%
Acetaldehyde	30.96%

Source: Measurement of Toxic air Pollutants from gasohol fuelled cars. Executive Summary, Pollution Control Department, April 2008.

2.20 Catalytic Converters

In the early history of emission control, hydrocarbons and carbon monoxide were reduces by a variety of engine modifications designed to improve combustion. The catalytic converters are after-devices that reduce emissions by combusting exhaust gases after they leave the combustion chamber. They are mounted before the muffler close to the engine manifold.

The term catalyst means helper. In this case it helps oxygen (O_2) to combine with carbon monoxide (CO) and unburned hydrocarbons (HC) to produce carbon dioxide (CO_2) and water (H_2O). Although the catalytic materials participate in combustion reactions, they do not undergo chemical conversion. In catalyzing combustion, the catalytic converter acts as incinerator. However, this incineration occurs at much lower temperatures (350-400°C) that is required for a thermal incineration (700-750°C) and consequently does not require supplemental energy source for efficient combustion. As combustion takes place in the converter, temperature may rise to over 500°C (Godish, T. 1991).

Two basic geometric configurations have been used in catalyst, namely the monolith design and the pellet design. Both designs use platinum, palladium and rhodium as catalytic materials. They may be used individually or in a platinum-palladium blend. Although these are more expensive than other catalytic converters, they have the advantage of not being affected by sulphur components in the gasoline. Due to its catalytic efficiency, less of these metals is required per vehicle.

The monolithic design catalytic converter, consists of a cylinder, 3-6 inches in diameter, which has an internal ceramic honeycomb structure as shown in Figure 2.3 whose surface is coated with the highly catalytic material.

The pellet design catalytic converter, consist of small pellets impregnated with catalytic material as shown in Figure 2.4. In both designs, there are thousands of passages which allow the exhaust gases to flow freely through the converter with relatively low back pressure. The high surface area allows the catalytic materials to come into direct contact with exhaust gases, oxidizing them to CO_2 and water vapor.

In addition to the converter itself, such system also utilize a quick heat intake manifold, electronic ignition, an air pump. Catalytic converters are least effective during cold start and engine warm up. A rich air-fuel mixture must be used during cold starts to compensate for the low volatility of cold fuel. This rich fuel mixture is not completely combusted and high emission of HC and CO in the exhaust pipes. In the quick heat intake system, air is drawn over the exhaust manifold where it is warmed to simulate summer ambient temperatures. The heating of the intake air improves fuel vaporization. The higher volatility of the fuel allows for leaner air-fuel engine operation and a shorter choking period during warm up.

The typical automobile exhaust gas catalyst is a (5:1) mix of platinum or palladium with rhodium, supported on an Al2O3 layer that is deposited on a ceramic base (de Nevers, N. 2000). The three way catalyst promotes the following reaction:

$$\mathrm{NO + CO + HC} \xrightarrow{\text{Platinum-Palladium-Rhodium catalysts}} \mathrm{N_2 + CO_2 + H_2O}$$

In the chemical and petroleum industries, the catalyst used is often prepared in the form of pellets slightly larger than an aspirin tablet. The most common catalyst is the honeycomb structure over a bed of pellets which is advantageous because it has a low pressure drop which force gases through it.

Since ethanol contains oxygen it can form corrosive agents especially to metals inside the catalytic converters. Although this process takes a significant amount of time before damage occurs, it is very important to closely inspect this device in order to avoid emission of toxic pollutants into the atmosphere especially formaldehyde and acetaldehyde.

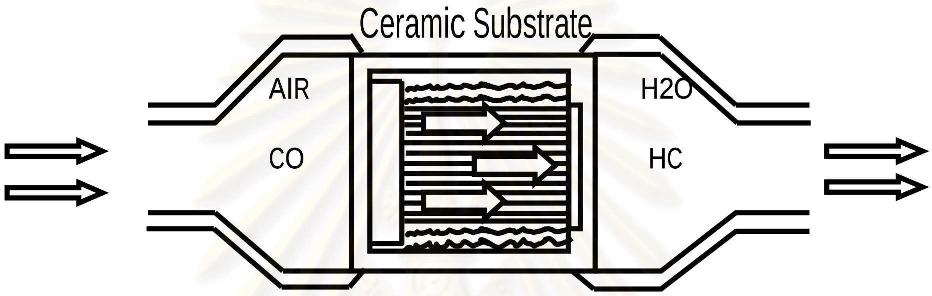


Figure 2.3 Catalytic Converter Monolithic Design

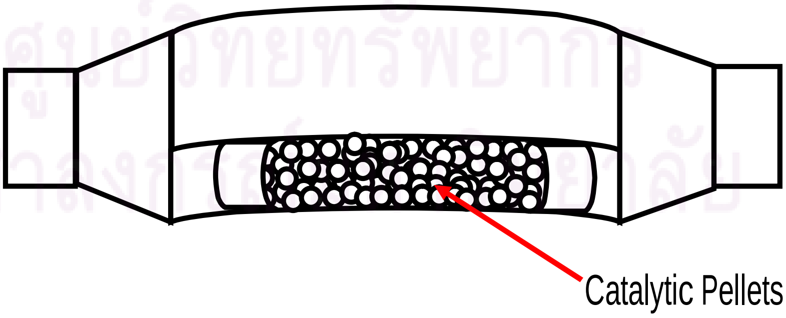


Figure 2.4 Catalytic Converter Pellet Design

CHAPTER III
RESEARCH METHODOLOGY

3.1 Details of the Area of Study

The area of study is Bangkok urban area. This city was chosen for this study because most of the gasohol refueling stations are located in Bangkok and the traffic density in this area is higher than any other cities in Thailand. The city is the 68th largest region in Thailand covering an area of 1,568.7 km^2 that lies about 2m above sea level which causes problems for the protection of the city against floods during monsoon season. Bangkok was named as 'Venice of the East' due to the number of canals and passages that divide the area into separate patches of land. The city once used these canals within Bangkok itself as divisions for city districts, however as the city started growing in the second half of the 20th century to large extents, the plan was abandoned and a different division. Geographical location of the Bangkok is 13° 45' N, 100° 31' E.

Bangkok has 50 districts each with a distinct specific difference in governance which all are under the control and authority of the Bangkok Metropolitan Administration. The city's main business districts and residential areas are ever expanding. The city has a registered 1000 skyscrapers and ranks 5th as the worlds tallest city. Areas such as Silom-Sathon and Asok have for decades been Thailand's business center. Bangkok's Phra Nakhon district has most governmental agencies and ministry head offices as well as the most famous tourist attractions due to the age of this particular area. This area is declared as a no-skyscraper designated zone to preserve some historic buildings as old as Thailand itself.

Bangkok’s population officially recorded on December 31, 1999 stood at 5,662,499, which is about 10% of the country's total population. In the year 2000 there were 6,355,144 registered residents here according to census which increased to 6,642,566 during the 2005 census, and the latest census was done on July 2007 which reported approximately 8,160,522 registered residents in Bangkok, due to large unregistered influxes of migrants from the North East of Thailand and of many nations across Asia, the population of greater Bangkok is estimated at nearly 15 million people. The half of population of Bangkok has Chinese ancestry in some way. The huge influx of immigrants, expatriates have contributed to make a Bangkok's population a vibrant one. Since Thai people, are well known for their friendly behavior and warmth hospitality. It is not likely that, Bangkok is one of the most often visited cities in Southeast Asia.

Several elevated highways, newly rebuilt intersections, and many partially finished roads and rail projects were constructed around greater Bangkok, but have done little to overcome the heavy traffic jams on Bangkok's roads as private vehicle usage continues to outstrip infrastructure development.

Bangkok also includes many shopping and business roads like the Sukhumvit Road which includes high rise business buildings, apartments, and shopping malls, Sukhumvit Road is where many foreigners like to come shopping. A regular bus service is provided by the Bangkok Mass Transit Authority (BMTA) and it operates throughout Bangkok as well as to adjoining provinces around the clock on certain routes. Public buses are plentiful and cheap, as wll as air-conditioned buses that goes everywhere within Bangkok. An elevated two-line Skytrain (officially called BTS) metro system is now in operation to the busy areas in Bangkok, likewise the MRT subway system is also open for use since 2004. It connects to the BTS system at BTS stations Mo Chit, Asoke, and Sala Daeng. Peak hours are between 6:30 am to 9:30 am and 4:30pm to 8:00 at night on weekdays, with a general state of traffic on Monday morning and Friday night.

3.1.1 The Geography and Meteorology of Bangkok

Bangkok is bordered by Samut Sakhon and Samut Prakan in the south, Nakhon Pathom to the west, Nonthaburi, Pathum Thani and Nakhon Nayok in the north, and Chachoengsao to the east and has a 4.4 km long coastline.

Bangkok has a tropical monsoon climate under the Köppen climate classification system. Absolute maximum temperature is 40.8 ◦C (105.4 ◦F) and absolute minimum temperature is 9.9 ◦C (49.8 ◦F). Bangkok's temperatures range from 77 degrees F at the height of winter to about 100 degrees F (25-35 degrees C) in summer March to June. Bangkok is said to have the highest average temperature of any city in the world. These temperatures go even worse even with the relative humidity at its lowest from November to February in the cold season at 60% and especially at its highest at over 80% during the summer's rainy season. Rainy season begin in mid June and continue through to October.

Table 3.1 Mean Temperature, Rainfall, and Prevalent wind direction in Bangkok.

DonMuang Airport	2007											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean Temperature (◦C) *	27.8	28.9	31.1	31.3	30.2	30.6	29.6	29.4	29.3	28.6	27.5	28.7
Rainfall (mm)	0.8	1.5	45.8	159	295	259	255	107	286	132	2.3	0
Bangkok Metropolis	2007											
Mean Temperature (◦C) *	28.4	29.1	31.5	31.9	30.3	30.8	29.9	29.7	29.5	29.0	28.1	29.4
Rainfall (mm)	29.9	0	12.7	143	310	268	270	147	262	226	17.6	0
Prevailing wind	S	S	S	S	S	W	W	W	W	N	N	N
DonMuang Airport	2008											
Mean Temperature (◦C) *	27.4	27.7	29.6	29.8	29.2	29.1	28.8	29.0	28.5	28.6		
Rainfall (mm)	5	16.7	0.7	91.7	314	211	122	186	283	287		
Bangkok Metropolis	2008											
Mean Temperature (◦C) *	27.8	27.9	29.6	30.3	29.3	29.3	28.7	29.1	28.5	28.6		
Rainfall (mm)	62.1	69.3	3.6	181	258	164	222	172	335	399		
Prevailing wind	S	S	S	S	S	W	W	W	W	N		

* Mean Temperature is the average of daily maximum and daily minimum

Source: Thai Meteorological Department. 2008

3.1.2 Photochemical Smog Pollution in the Bangkok in Relation to O_3 precursor Concentrations and Meteorological Conditions

Analysis of photochemical pollution was done by B-N Zang et al in 2002, using the available 5-yr monitoring data (1996–2000) from 11 monitoring stations in Bangkok and 5 stations in other surrounding provinces, i.e. the Bangkok Metropolitan Region (BMR). Status and trend of O_3 as well as the monthly and diurnal variations in relation to the local meteorological conditions and regional transport of pollutants associated with the monsoon. The O_3 in Bangkok was found to be typical for the polluted urban areas with a lower concentration in the city center, especially at curbside stations, and higher concentration at the downwind locations. O_3 pollution was highest in 1997 with the maximum hourly average of 370 ppbv and the total hours exceeding the national hourly O_3 standard (100 ppbv) of 314 h, which is most likely related to the strong El Niño and the forest fire in Southeast Asia during that year. Meteorology-unadjusted trend showed slight increase in O_3 from 1998 to 2000. The study, concluded that local emission and photochemistry are mainly responsible for O_3 episodes in the BMR. Seasonal fluctuations of O_3, were found to relate to the regional transport associated with the Asian monsoon. Highest O_3 pollution was found in the period from January to April (winter and local summer) and lowest during mid-rainy season, August. Based on their study the O_3 increase isopleth diagram showed that O_3 production in BMR is effective when the NO_x/NMHC ratio was in the range of 0.04 to 0.15 with optimum ratio at around 0.07. Seasonal variations in NO_x/NMHC ratios are consistent with the O_3 variations, optimum in summer (0.07), followed by winter (0.05), and the lowest in rainy season (0.03).

3.1.2 Ambient Air Quality Standards in Thailand

The first act for the control and conservation of national environmental quality in Thailand was the Enhancement and Conservation of National Environmental Quality Act of 1975 which established the Office of the National Environment Board. The Act of 1975 was repealed and the Enhancement and Conservation of National Environmental Quality Act of 1992 which was promulgated and published in the Royal Gazette in 1992 and became effective on the same year. In 1995, the Pollution Control Department revised the 1981 primary ambient air quality standards, under Section 32 of the

Enhancement and Conservation of National Environmental Quality Act of 1992. The revised standards were gave importance on the latest information on human health impact of key pollutants such as carbon monoxide, nitrogen dioxide, sulphur dioxide, total suspended particulates, particulate matter, lead, and ozone within the constraints of specific environmental, socio-economic, and technological conditions that exist in Thailand. Table 3.2 shows the current National Primary Ambient Air Quality Standards (NPAAQS). Recently, the Pollution Control Department launched a new Volatile Organic Compounds (VOCs) Ambient Air Quality Standards for Thailand. Table 3.3 shows the Volatile Organic Compounds (VOCs) Ambient Air Quality Standards for Thailand.

Table 3.2. Ambient Air Quality Standards for Thailand

Ambient Air Quality Standards for Thailand		
Pollutants	Time	Standards
Carbon Monoxide (CO)	1 hr	Not exceed 30 ppm (34.2 mg/m^3)
	8 hr	Not exceed 9 ppm (10.26 mg/m^3)
Nitrogen Dioxide (NO2)	1 hr	Not exceed 0.17 ppm (0.32mg/m^3)
Ozone (O3)	1 hr	Not exceed 0.10 ppm (0.20mg/m^3)
	8 hr	Not exceed 0.07 ppm (0.14mg/m^3)
Sulfur Dioxide (SO2)	1 hr	Not exceed 0.3 ppm (780μg/m^3)
	24 hr	Not exceed 0.12 ppm (0.30mg/m^3)
	1 year	Not exceed 0.04 ppm (0.10mg/m^3)
Lead (Pb)	1 month	Not exceed 1.5μg/m^3
Particulate Matter (<10μ) (PM-10)	24 hr	Not exceed 0.12 mg/m^3
	1 year	Not exceed 0.05 mg/m^3
Particulate Matter (<100μ)	24 hr	Not exceed 0.33 mg/m^3
	1 year	Not exceed 0.10 mg/m^3

Source: Pollution Control Department, 2008

Table 3.3 Volatile Organic Compounds (VOCs) Ambient Air Quality Standards for Thailand, 2008

Volatile Organic Compounds (VOCs) Ambient Air Standards for Thailand		
	Pollutants	Standards
1	Benzene	Not exceed 1.7 $\mu g/m^3$
2	Vinyl Chloride	Not exceed 10 $\mu g/m^3$
3	1,2- Dichloroethane	Not exceed 0.4 $\mu g/m^3$
4	Trichloroethylene	Not exceed 23 $\mu g/m^3$
5	Dichloromethane	Not exceed 22 $\mu g/m^3$
6	1,2- Dichloropropane	Not exceed 4 $\mu g/m^3$
7	Tetrachloroethylene	Not exceed 200 $\mu g/m^3$
8	Chloroform	Not exceed 0.43 $\mu g/m^3$
9	1,3- Butadiene	Not exceed 0.33 $\mu g/m^3$

Source: Pollution Control Department, 2008

3.2 Method Validation

This study followed the United States Environmental Protection Agency (U.S. E.P.A.) Method TO -11A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (Active Sampling Methodology) as guideline. There were 15 carbonyl compounds measured, namely: formaldehyde, acetaldehyde, acetone, acrolein, crotonaldehyde propionaldehyde, butyraldehyde, benzaldehyde, Isovaleraldehyde, Valeraldehyde, o-toualdehyde, m-tolualdehyde, p-Tolualdehyde, Hexanaldehyde, and 2,5 Dimethylbenzaldehyde. Table 3.4 shows names, molecular formula, constituent element, and molecular formula of the 15 carbonyl compounds studied. Figure 3.1 shows the chromatogram of the 15 carbonyl compounds.

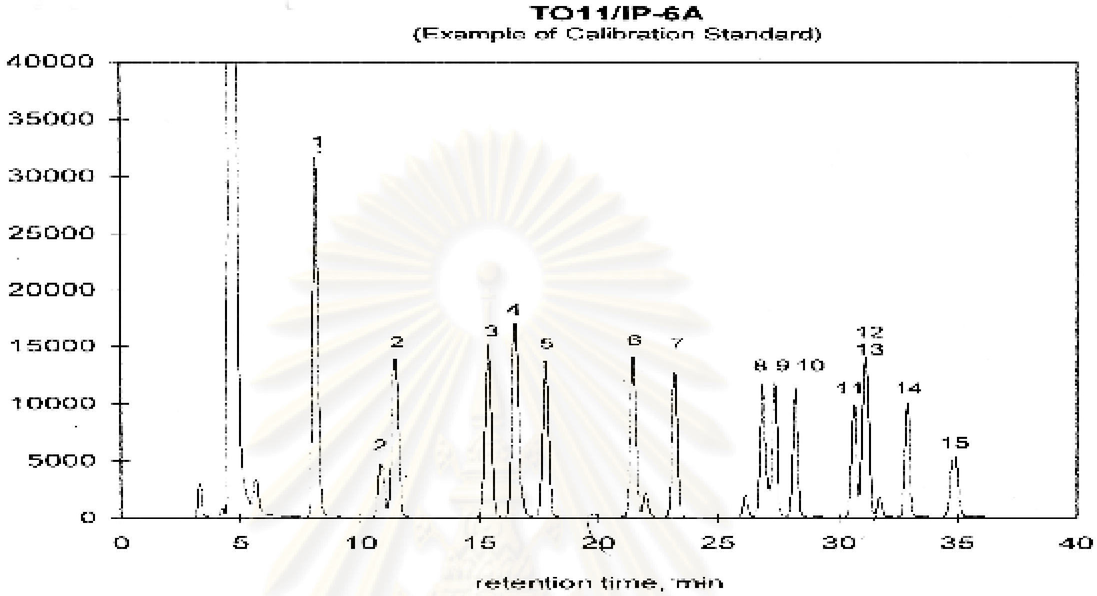


Figure 3.1 Chromatogram 15 carbonyl compounds

Table 3.4. Fifteen carbonyl compounds with their respective molecular formula, and molecular weight.

Carbonyl compounds	Molecular Formula	constituent element			Molecular Weight
		H	C	O	
Formaldehyde	H_2CO	2	1	1	30.03
Acetaldehyde	H_4C_2O	4	2	1	44.05
Acetone	H_6C_3O	6	3	1	58.08
Acrorein	H_4C_3O	4	3	1	56.06
Propionaldehyde	H_6C_3O	6	3	1	58.08
Crotonaldehyde	H_6C_4O	6	4	1	70.09

Butylaldehyde	H_8C_4O	8	4	1	72.10
Benzaldehyde	H_6C_7O	6	7	1	106.12
Isovaleraldehyde	$H_{10}C_5O$	10	5	1	86.13
Valeraldehyde	$H_{10}C_5O$	10	5	1	86.13
o-Tolualdehyde	H_8C_8O	8	8	1	120.14
m-Tolualdehyde	H_8C_8O	8	8	1	120.14
p-Tolualdehyde	H_8C_8O	8	8	1	120.14
Hexaldehyde	$H_{12}C_6O$	12	6	1	100.16
2,5-Dimethylbenzaldehyde	$H_{10}C_9O$	10	9	1	134.17

3.2.1 Principle of Sampling by using DNPH Cartridge

Air is drawn through a cartridge which contains 2,4 Dinitrophenylhydrazine (2,4-DNPH) coated silica packed in a polyethylene tube. Aldehydes react with the acidified 2,4-DNPH to form the corresponding hydrazones derivative according to the reaction shown in Figure 3.2. After exposure the cartridge are eluted with acetonitrile, and the sample extract is analyzed by HPLC equipped with a UV detector. The detection and quantification is carried out at 360 nm.

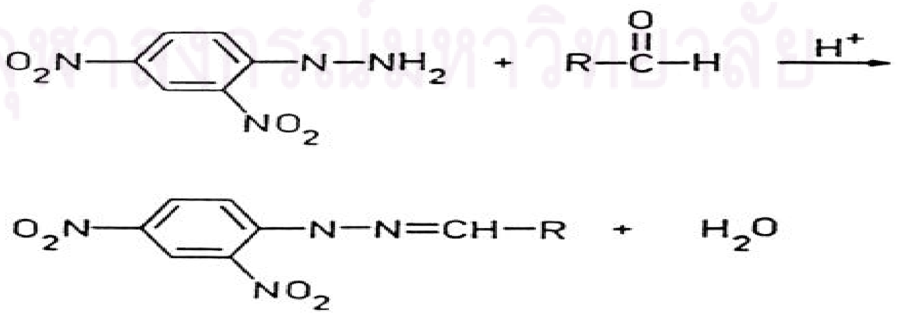


Figure 3.2 Reaction scheme of aldehydes with DNPH.

3.2.2 Passive Sampling for Carbonyl Compounds

Passive sampling is the collection of airborne gases and vapors at a rate controlled by physical process such as diffusion (without the use of pumps). Passive (diffusive) sampling rely on the movement of contaminant molecules across a concentration gradient, such as molecules diffuse from an area of high concentration in air to an area of low concentration on the sampler. Although most studies of ambient VOCs particularly carbonyl compounds have been performed with active samplers that requires a power supplied mini air pump to collect a precise volume of air in a given period of time, it is difficult to survey many points simultaneously because it requires the use of electricity. Passive samplers can be used where electricity is not available and because it is small and silent it is very useful for measuring personal exposures and analyzing both indoor and outdoor air. In addition, passive samplers can be produced inexpensively and used to investigate many sampling points and locate emission sources in a particular area. However, application of passive samplers for collection of carbonyl compounds have been limited to carbonyls at relatively high concentration such as formaldehyde, acetaldehyde, because the sampling rate of passive sampler is approximately 1/20 that of an active sampler (Lewis et al., 1986c, Mulik et al., 1989, Sakai et al., 2004). The passive samplers provide time-integrated concentrations with continuous time coverage, with the averaging time determined by the period they are exposed to ambient air , which can be hourly, daily, weekly, monthly, etc.

Under this study, the researcher used the DSD-DNPH passive cartridge sampler by SUPELCO Company, for collecting ambient air in Bangkok, because it allows collection and analysis of carbonyls without transfer of the adsorbent, which minimizes the risk of contamination .Due to its high-purity adsorbent provides collection of ppb levels of a wide range of carbonyls in a convenient, easy-to-use configuration. The DSD-DNPH diffusive sampler was introduced first in Japan and was an integral device for monitoring carbonyls in air.

The DSD-DNPH sampler is comprised of a porous polyethylene tube, which acts as the diffusive membrane, to which is attached a small polypropylene syringe used for the elution of the analytes from the adsorbent. Because the diffusive membrane is round, it permits exposure from all sides, making it unique compared to other diffusive samplers. Silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) acts as the adsorbent and moves from the diffusive end during sample collection to the syringe end for sample extraction, by inverting the device, Aldehydes and ketones diffuse through the membrane reacting with DNPH to form stable derivatives. The DNPH-derivatives are then eluted with acetonitrile and analyzed by high performance liquid chromatography (HPLC). Figure 3.3 shows the picture of the DSD-DNPH passive cartridge.

Figure 3.3. DSD-DNPH passive cartridge

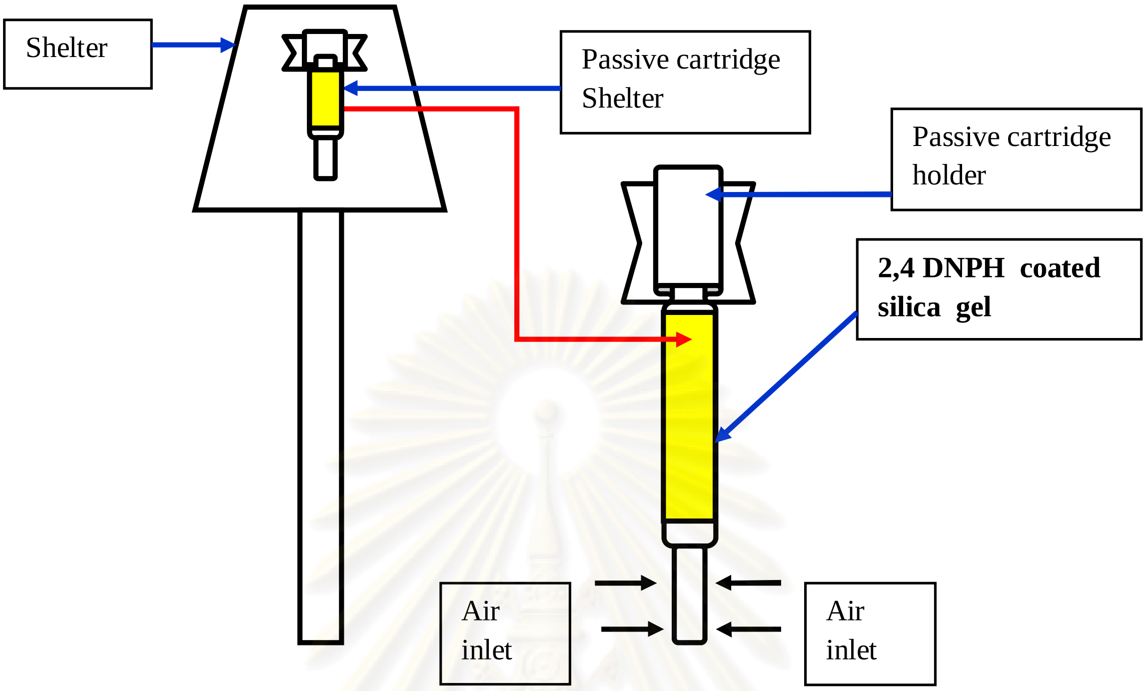


Figure 3.4 Schematic diagram of passive sampling

Figure 3.5. Sampling by DNPH passive sampler

3.2.3 Sampling Procedures by DNPH passive sampler

Under this study the researcher used the DSD-DNPH passive sampler cartridge commercially available in Thailand for collecting ambient air for analysis of carbonyl compounds. The manufacturer of this passive sampler is SUPELCO company. The sampling procedure is shown in Figure 3.6 below.

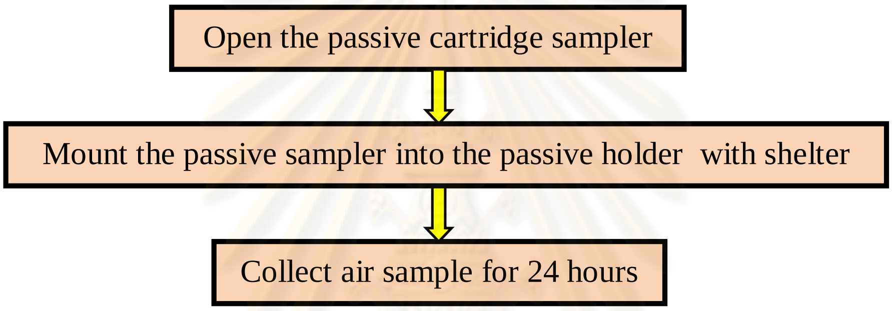


Figure 3.6 Sampling Procedures for carbonyl compounds using DNPH passive sampler

3.2.4 Extraction procedures for passive samples

The extraction procedures for passive air samples applied the method recommended by the manufacturer (SUPELCO company for DSD-DNPH passive sampler) . The procedure was easy and less time consuming. However, extra care should be applied in order to avoid contamination during the extraction process. The solvent used was HPLC grade acetonitrile produced by WAKO company, Japan. The extraction procedures is shown in Figure 3.7.

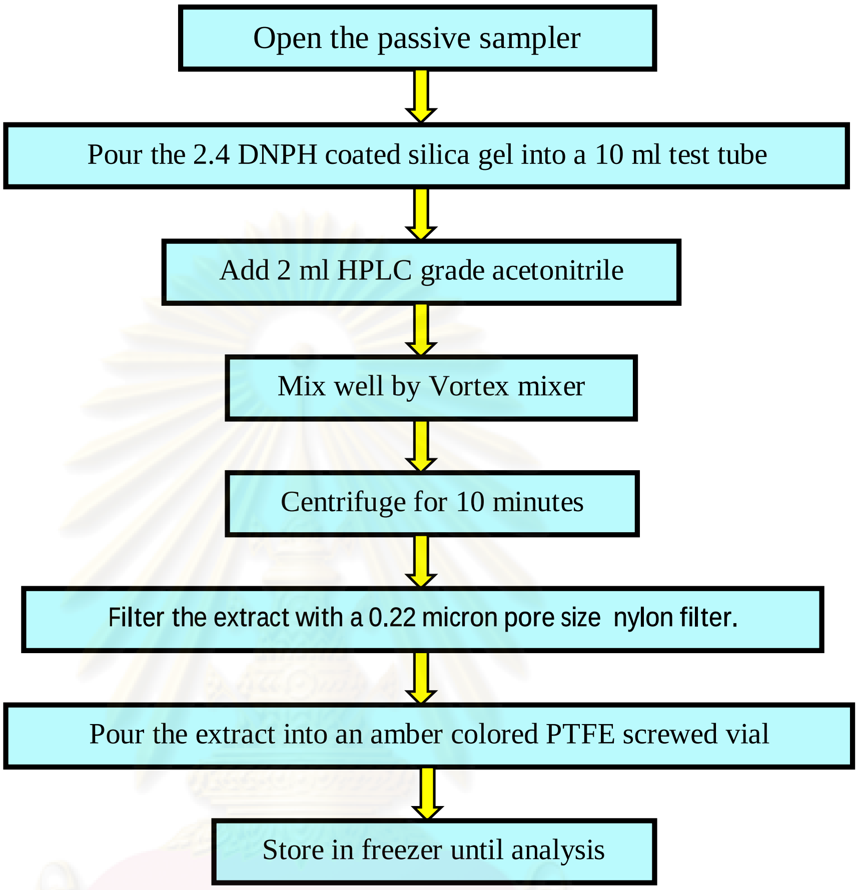


Figure 3.7 Extraction procedures for DNPH passive sampler

3.2.5 Active Sampling for Carbonyl Compounds

Active sampling involves the collection of air to be analyzed through a sampling tube or probe using a pump. The compounds of interest accumulate on the sorbent material in the tube and are returned to the laboratory for analysis, giving a result as “mass per tube”. The volume of air passed through the sorbent or collection device is also accurately determined (i.e. cubic meters). The active sampling technique is suitable for sampling carbonyl compounds because a large volume of ambient air can be precisely collected by using a pump, which in turn makes sufficient amount of target substances available for accurate quantitative analysis. However, active sampling especially for long term exposure is often impossible because of limited lifetime of battery, noise, weight of pumps, and adsorption capacity of cartridge. Most studies of ambient VOCs particularly carbonyl compounds have been performed with active samplers that requires an air pump and power supply. Although active sampling have the advantage to collect precise volume of air in a given period of time, it makes it difficult to survey many points simultaneously because it requires the use of electricity. Artifact problems may interfere when using active samplers for collection of carbonyl compounds in atmospheres containing relatively high ozone levels.

Figure 3.8 DNPH active cartridge

Figure 3.9 Sampling by DNPH active sampler.

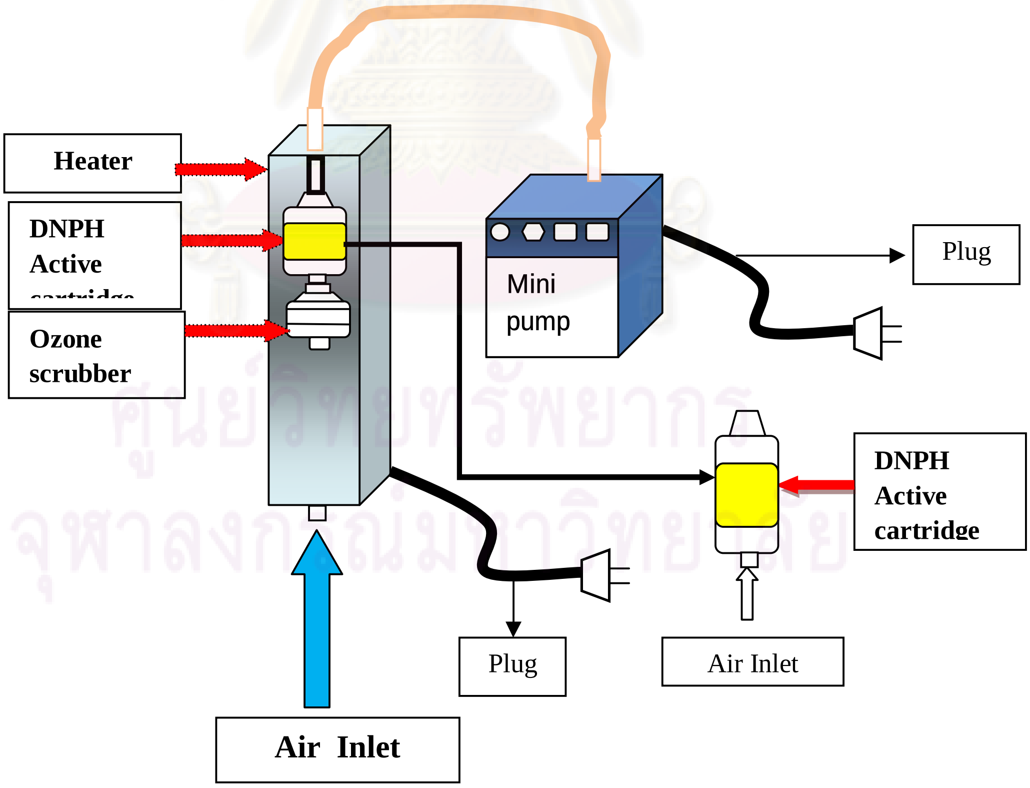


Figure 3.10 Schematic diagram of active sampling

3.2.6 Sampling Procedures for Carbonyl Compounds by using DNPH active sampler.

Under this study the researcher used the Wako active sampler cartridge commercially available in Thailand for collecting ambient air for analysis of carbonyl compounds. The manufacturer of this passive sampler is Wako company in Japan. The sampling procedure is shown in Figure 3.11 below.

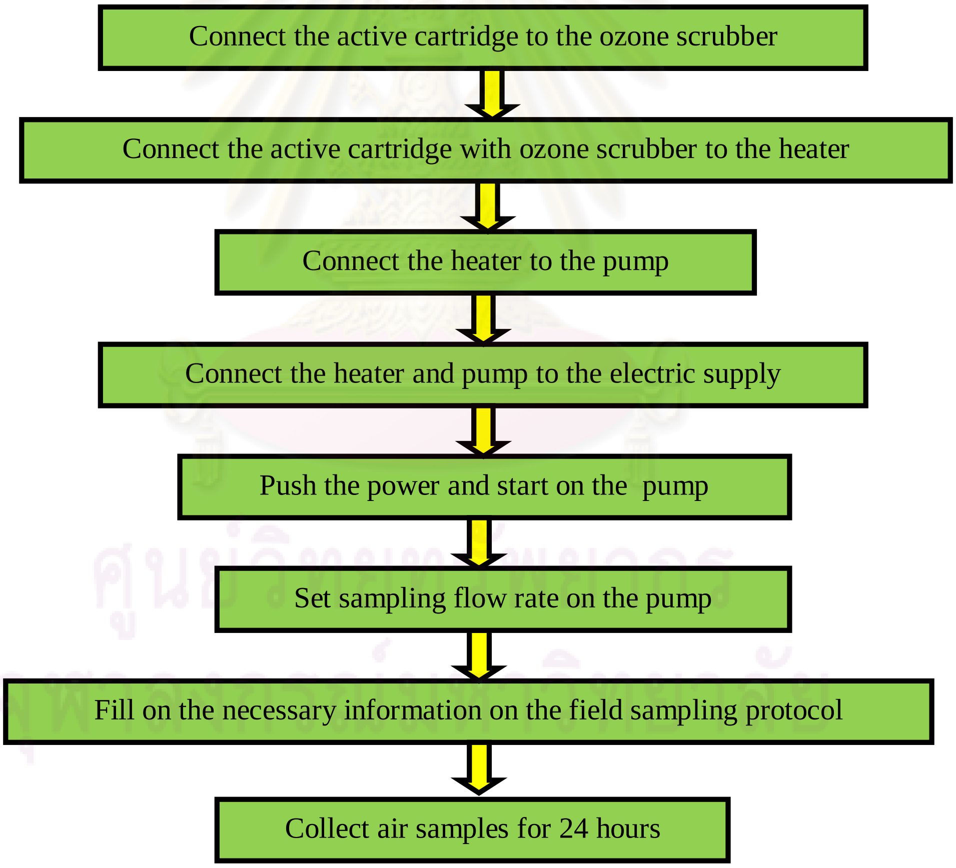
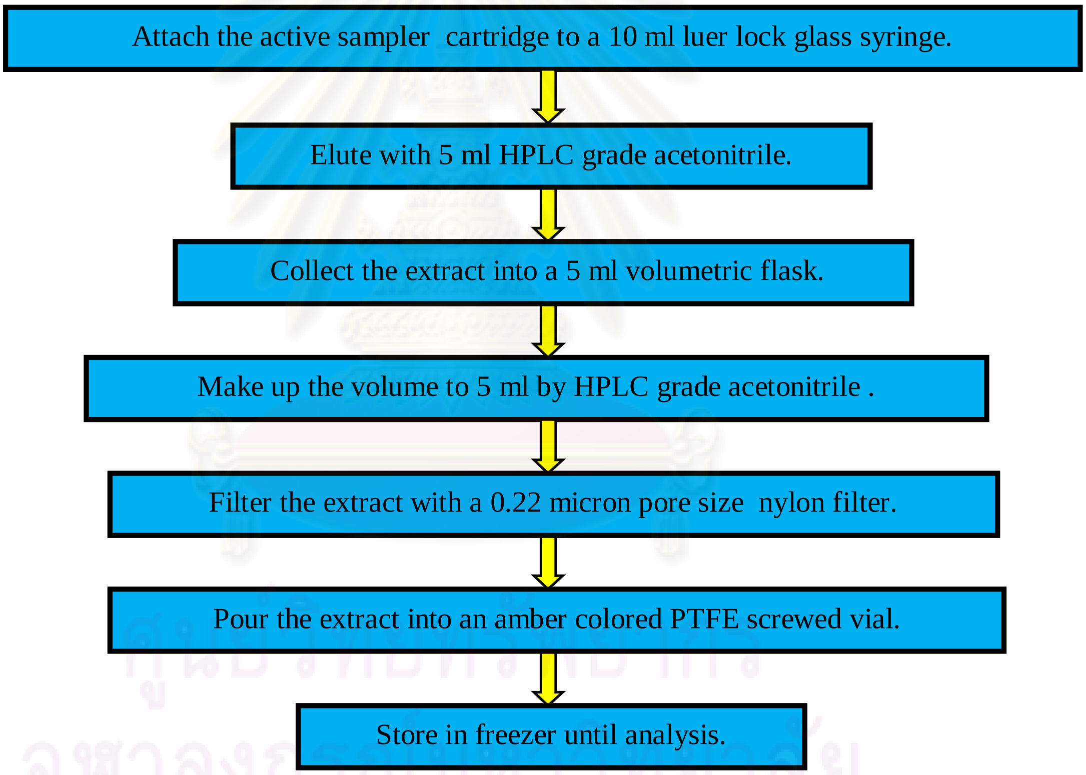


Figure 3.11 Sampling procedures for carbonyl compounds by DNPH active sampler

3.2.7 Extraction procedures for DNPH active sampler

The extraction procedures for passive air samples applied the method recommended by the manufacturer (SUPELCO company for DSD-DNPH passive sampler) . The procedure was easy and less time consuming. However, extra care should be applied in order to avoid contamination during the extraction process. The solvent used was HPLC grade acetonitrile produced by WAKO company, Japan. The extraction procedures is shown in Figure 3.12.


Attach the active sampler cartridge to a 10 ml luer lock glass syringe.

Elute with 5 ml HPLC grade acetonitrile.

Collect the extract into a 5 ml volumetric flask.

Make up the volume to 5 ml by HPLC grade acetonitrile .

Filter the extract with a 0.22 micron pore size nylon filter.

Pour the extract into an amber colored PTFE screwed vial.

Store in freezer until analysis.

Figure 3.12 Extraction Procedures for DNPH active sampler

3.2.8 DNPH Cartridge Selection

There are various manufacturers of DNPH cartridge. Some DNPH cartridge contain a certain concentration of carbonyl compounds. It is therefore very important to select the best cartridge used for sampling by measuring the concentration of carbonyl compounds in cartridge supplied by different manufacturers. In this study, the researcher purchased DNPH active cartridge from 4 manufacturers namely: SUPELCO company, WAKO company, Waters company, and G.L. Science company. Three active cartridges were analyzed from each manufacturer. The concentrations of carbonyl compounds measured were compared. The cartridge from WAKO company had the lowest concentration of carbonyl compounds. The comparison of the results is shown Table 3.5.

Table 3.5 Result of blank test using DNPH active cartridges from 4 manufacturers

ALDEHYDE (ug/Cartridge)	Supelco Ave. blk	Wako Ave. blk	GL. SCIE. Ave. blk	Waters. Ave. blk
Formaldehyde	0.012	0.005	0.005	0.005
Acetaldehyde	0.052	0.012	0.016	0.008
Acetone	0.031	0.010	0.016	0.039
Acrolein	0.011			
Propionaldehyde	0.091			0.005
Crotonaldehyde		0.006		0.013
Butyraldehyde	0.011		0.005	

	Supelco	Wako	GL. SCIE.	Waters.
ALDEHYDE (ug/Cartridge)	Ave. blk	Ave. blk	Ave. blk	Ave. blk
Benzaldehyde	0.313			
Isovaleraldehyde			0.005	
Valeraldehyde				
o-Tolualdehyde				
m,p-Tolualdehyde	0.012			0.012
Hexaldehyde	0.012			0.012
2,5-Dimethylbenzaldehyde				

3.2.9 Recovery test

Recovery test is very important process to evaluate the capacity of a certain cartridge to collect and retain the analyte collected. Under this study, recovery test was performed by injecting 100 μL of 0.5 ppm mix standard solution of carbonyl compounds into a blank cartridge. The cartridge were extracted the same procedure as the samples. A minimum of three cartridge from each manufacturer were used under this test. The result of recovery test is shown in Table 3.6.

Table 3.6 Result of recovery test

ALDEHYDE (ug/Cartridge)	Supelco %Recovery	Wako %Recovery	GL Scie %Recovery	Waters %Recovery
Formaldehyde	123	101	101	108
Acetaldehyde	167	80	75	82
Acetone	137	103	113	126
Acrolein	105	84	83	86
Propionaldehyde	243	85	76	82
Crotonaldehyde	70	69	71	70
Butyraldehyde	84	72	69	76
Benzaldehyde	210	89	88	88
Isovaleraldehyde	86	90	83	91
Valeraldehyde	79	73	70	76
o-Tolualdehyde	85	84	80	86
m,p-Tolualdehyde	103	84	78	86
Hexaldehyde	86	78	77	92
2,5-Dimethylbenzaldehyde	76	83	79	83

3.2.10 Determination of IDL and IQL

The Instrument Quantification Limit (IQL) and Instrument Detection Limit (IDL) were determined by preparing 0.03 mg/l of mix standard carbonyl compounds. Inject into the HPLC system for 7 times. The average value, standard deviation (SD), and %RSD were calculated. The IDL of each compound were determined from 3SD, and the IQL were obtained from 10SD. The value of IQL was used as the Not Detected (ND) for each compound quantified. The result of IDL and IQL test is shown in Table 3.7.

Table 3.7 Result of IDL and IQL test

Aldehydes	Average	SD	3SD (IDL)	10SD (IQL)
Formaldehyde	0.030	0.000	0.000	0.000
Acetaldehyde	0.028	0.000	0.001	0.004
Acetone	0.031	0.000	0.001	0.004
Acrolein	0.030	0.000	0.001	0.004
Propionaldehyde	0.031	0.000	0.001	0.004
Crotonaldehyde	0.027	0.001	0.004	0.012
Butyraldehyde	0.029	0.001	0.002	0.006
Benzaldehyde	0.024	0.001	0.002	0.005
Isovaleraldehyde	0.028	0.000	0.001	0.005
Valeraldehyde	0.031	0.001	0.002	0.006
o-Tolualdehyde	0.030	0.000	0.001	0.005
m,p-Tolualdehyde	0.021	0.000	0.000	0.000
Hexanaldehyde	0.027	0.000	0.001	0.005
2,5-Dimethylbenzaldehyde	0.030	0.000	0.001	0.004

3.2.11 The effect of ozone to the concentration of carbonyl compounds during sampling.

Air constituents like ozone and nitrogen oxides can react with the DNPH and carbonyl compounds to form unwanted artifacts that can cause negative biases. In order to eliminate these interferences, ozone scrubber should be attached to the active cartridge to trap ozone interference and moisture during sampling. The potential influence of ozone to DNPH active cartridge samplers was investigated by the cartridge manufacturers as shown in Table 3.8.

Table 3.8 Effect of ozone to carbonyl compounds during sampling.

Sample	FORMALDEHYDE (μg/ml)		ACETALDEHYDE (μg/ml)	
	With Ozone Scrubber	Without Ozone Scrubber	With Ozone Scrubber	Without Ozone Scrubber
Sample 1	3.61	1.51	5.53	0.83
Sample 2	5.13	1.12	2.37	0.45

Source: GL. Science, 2007

To meet the objectives of this study, several tasks has been performed as follows:

Task 1:

3.3 Conduct Preliminary Survey for Carbonyl Compounds in Bangkok

The study of carbonyl compounds in Bangkok was very limited. The researcher cannot find any research results concerning the prevalent carbonyl compounds as well as their level of concentration in Bangkok. Therefore, a preliminary survey was conducted in March 2006 at 49 sites in Bangkok urban area. The selected area was 7 by 7 kilometers inside Bangkok busy areas. Passive sampler was used to collect samples because it is convenient to use in monitoring many sites. All of the sampling sites were located near the roadside. The sampling duration was 24 hours. The GPS information were recorded from each site. After collection, the samples were brought to the laboratory for extraction and analysis.

3.3.1 Sampling Locations

The concentration of air pollutants differs depending on the location and time. The measured value of each pollutant in a given sampling site must be representative of the area of study. However, pollutant concentrations at each sampling point changes in accordance with the existence of local pollution sources, geographical features of the area, meteorological conditions, and many other factors. Thus, measurement should be representative of the area to minimize complications during the interpretation of data.

By using the 7km x 7km area in Bangkok, the researcher divided the areas to 1km x 1km grit. One sample was collected from each grit. Since the area was 7km^2 the number of samples collected were 49 samples. The map of the sampling site for preliminary survey is shown in Figure 3.13, and the names of the sampling sites with their corresponding GPS information is shown in Table 3.7.

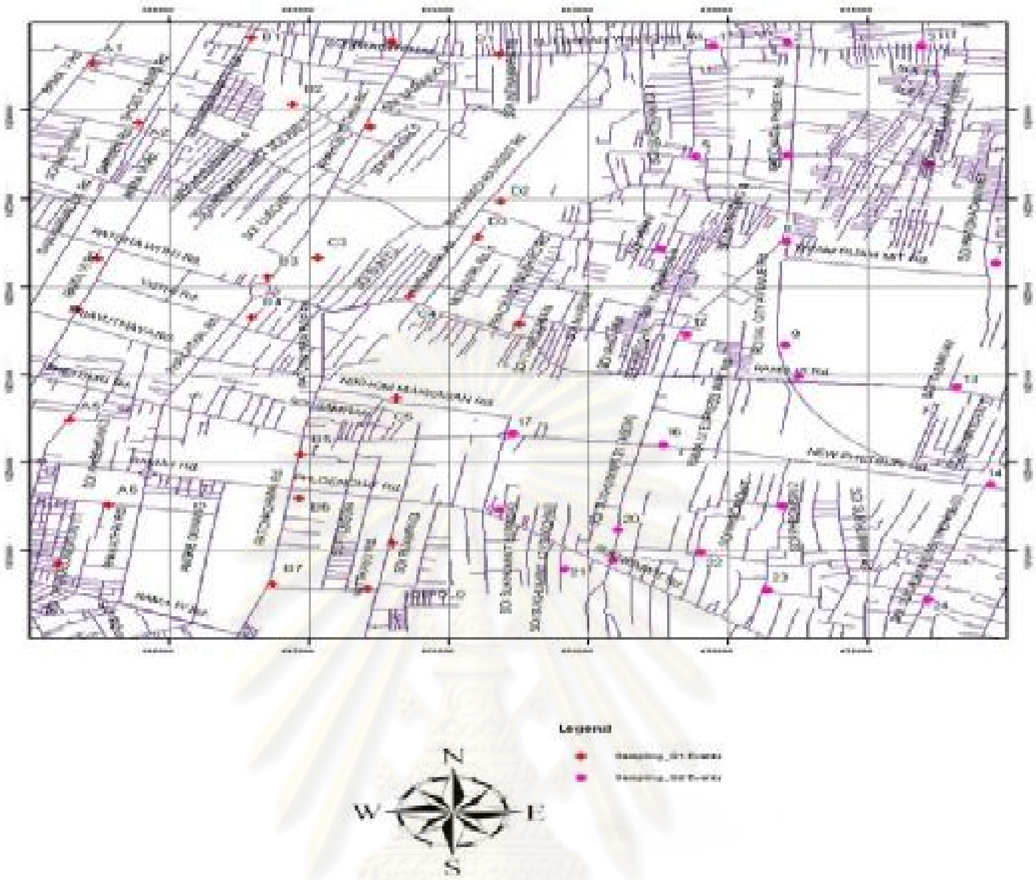


Figure 3.13 Map of sampling sites for preliminary survey

Table 3.9 Names of the 49 sites with their GPS information monitored for preliminary survey of carbonyl compounds in Bangkok.

No.	UTM		Location
	X	Y	
1	665071	1524805	Ranong (Dusit Police station)
2	665400	1524142	Samsen Train station
3	665108	1522594	Rama Hospital Intersection
4	664967	1522011	Ministry of Science Intersection
5	664910	1520759	Shell Gas station Banthadthong
6	665178	1519789	Chulalongkorn

No.	UTM		Location
	X	Y	
7	664820	1519116	Chulalongkorn soi 36
8	666206	1525096	Rama 6 Intersection
9	666507	1524342	Dept. of Environmental Quality Promotion
10	666325	1522380	Victory Monument
11	666210	1521925	Century Dept. Store
12	666560	1520365	Big C World Trade
13	666550	1519865	Erawan Hotel
14	666366	1518896	Rachadamri Intersection
15	667207	1525057	Pradiphat
16	667062	1524093	Soi Aree
17	666680	1522604	Army Cooperative Store
18	667345	1522174	Dindaeng Intersection (Police Station)
19	667252	1521003	Makkasan Train station
20	667223	1519352	Association of Thai Industry
21	667045	1518845	Bangkok Radio Broadcast Station
22	667981	1524911	Bang Chak gas station (Suthisan)
23	667994	1523238	PTT gas station (Suthisan)
24	667837	1522837	Vipawadee Rangsit Park
25	668128	1521845	PCD Monitoring station (Dindaeng)
26	669511	1525019	Soi Inthamara 30
27	670050	1525055	Suthisan Intersection
28	671006	1525012	Suthisan Rd.
29	670047	1523767	Huay Kwang Intersection
30	669394	1523755	Huay Kwang Market
31	671057	1523666	Prachabumroong Rd.
32	671540	1522545	Thiyab ruammit Rd.

No.	UTM		Location
	X	Y	
33	670038	1522791	Cultural Center Intersection
34	670032	1521609	Near Subway Repair and Maintenance Office
35	670130	1521260	Phang Muang Intersection
36	669136	1522705	Soi Prani
37	669320	1521735	Opposite Fortune Dept. Store
38	671254	1521141	Soi Yaemnang
39	671508	1520024	Thonglor-Pechburi Intersection
40	670014	1519780	Soi Prosiri 2
41	669150	1520479	Jica office
42	668074	1520603	Mith Sampan Intersection
43	667983	1519737	Nana Intersection
44	668798	1519164	Asoke Intersection
45	668837	1519504	Asoke Rd.
46	668458	1519064	Sukumvit 12
47	669426	1519261	Sukumvit 33
48	669900	1518829	Sukumvit 39
49	671049	1518709	Soi Thonglor 15

3.3.2 Sample Collection

For the preliminary survey a diffusive sampling device (DSD-DNPH passive sampler) has been used for collection of carbonyl compounds for 24 hours in Bangkok ambient air. The DNPH passive sampler is comprised of silica gel coated with 2,4-dinitrophenylhydrazne (DNPH) as the absorbent, a porous sintered polyethylene tube (PSP-diffusion filter) which acts as a diffusive membrane, and a small polypropylene syringe (PP-reservoir) which s used for the elution of the analytes from the absorbent. As the diffusive membrane comprises the entire cylindrical surface of the tube, it allows radial exposure from all sides. The manufacturer of this passive sampler is SUPELCO company. The appearance of the DNPH passive cartridge is shown in Figure 3.3. Sampling for carbonyl compounds using DNPH passive sampler is shown in Figure 3.5

3.4 Separation and Analysis

The extraction procedures for passive air samples applied in this study followed the procedures done by (Kume et al., 2000). The procedure was easy and less time consuming. However, extra care should be applied in order to avoid contamination during the extraction process. The solvent used for extraction was HPLC grade acetonitrile produced by WAKO company, Japan. The extraction procedures is shown in Figure 3.7.

The separation and analysis for carbonyl compounds in ambient air was done by using a Shimadzu High Performance Liquid Chromatography (Japan) with UV-VIS detector Shimadzu SPD 20A, the Integrator is Shimadzu CBM 20A. The mobile phase is pumped into the system by Shimadzu LC pumps AB20 and the mobile phase used were HPLC grade acetonitrile and high purity HPLC grade water both produced by Fisher Company, Canada. The solvents were filtered with 0.22μm pore size, nylon filters (Advantec, USA) before use. The solvents used were freshly prepared for every analysis. The oven is Shimadzu CTO 20AC which is set at temperature of 40°C during analysis. The carbonyl compounds were separated by a column RP Amide Discovery C16 250 cm x 4.6 mm i.d. with 0.5 μm packing from SUPELCO Company, USA. The schematic diagram of the HPLC system is illustrated in Figure 3.14. The samples flows into the system by the pump through a linear gradient program. The analytical condition for the analysis of carbonyl compounds by HPLC is shown in Table 3.10.

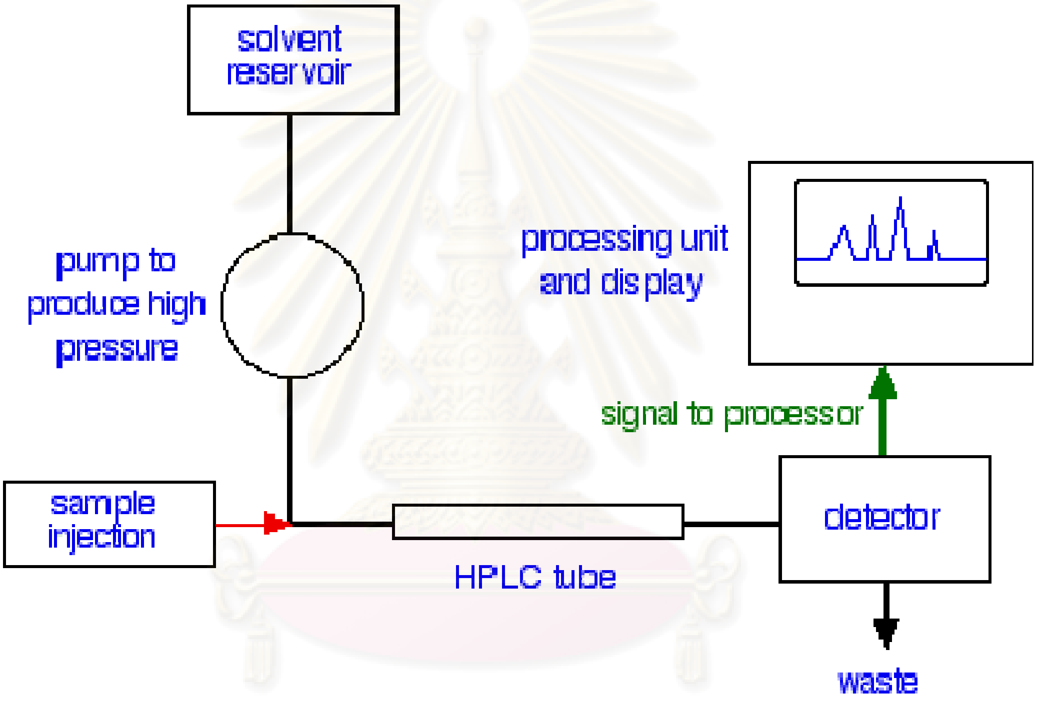


Figure 3.14 Schematic diagram of HPLC

Table 3.10 Analytical condition for analysis of carbonyl compounds

Main Column	RP Amide Discovery C16 250 cm x 4.6 mm i.d. with 0.5 μm packing
Pre- Column	RP Amide C16 2 cm x 4.0 mm i.d. with 0.5 μm packing
Mobile Phase	A: WaterHPLCgrade (45%) B: Acetonitrile HPLC grade (55%)
Column Temperature	40°C
Flow rate	1.0 ml/min
Detector	UV detector
Wavelength	360 nm
Injection volume	25 μL
Gradient Program	Time (min)
Acetonitrile : 55%	20
Acetonitrile 65%	5
Acetonitrile 55%	5

3.5 Calibration curve

Calibration curve are usually constructed before analysis of samples. In this study, a 5 point calibration curve was prepared. The calibration curve is useful for the quantification of the level of carbonyl compounds in the atmosphere. The reliability of the calibration curve need to be clarified. The $r^2 \geq 0.996$ for every compound, and the %RSD for each compound should be within 10%. The range of concentration used in this study was 0.01, 0.05, 0.10, 0.50, and 1.0 mg/l mix standard solution of 15 carbonyl compounds.

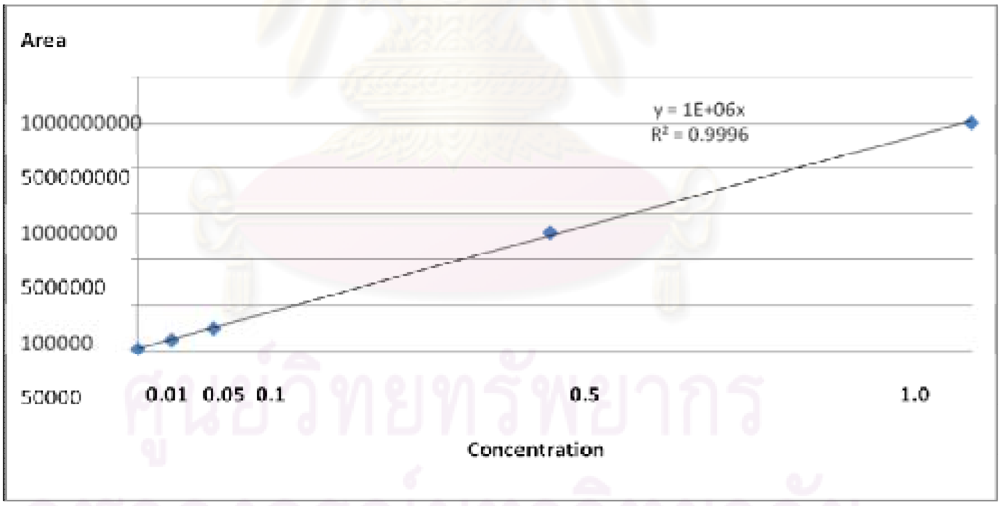


Figure 3.15 Calibration curve of Formaldehyde

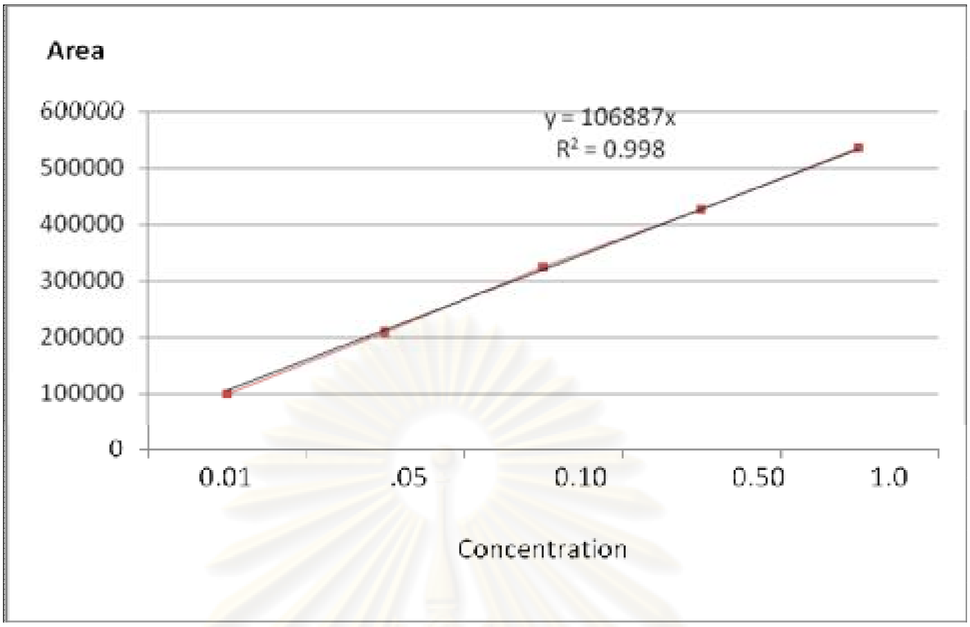


Figure 3.16 Calibration curve of Acetaldehyde

3.6 Quantification of passive samples

In the calculation of passive samples, the equation below was used. Since there were no pumps used to obtain the sampling flow rate. Therefore, the amount of air collected during the sampling period could not be determined. In this case the sampling rate used for the calculation of the concentration of carbonyls was supplied by the manufacturer of the passive sampler, (SUPELCO, Company, USA). Table 3.9 shows the sampling rate supplied by SUPELCO Company.

$$\mu g/m^3 = \frac{\mu g \text{ concentration from analysis} - \text{blank} \times (\text{final volume})}{\text{sampling rate (L/min)} \times \text{sampling time (min)}} \times 1000$$

Table 3.11 Sampling rate for DNPH passive sampler

Compound	Molecular Weight	Sampling rate
Formaldehyde	30.03	71.9
Acetaldehyde	44.05	59.4
Acetone	56.06	52.6
Acrolein	58.08	51.7
Propionaldehyde	58.08	51.7
Crotonaldehyde	70.09	47.1
Butyraldehyde	72.11	46.4
Benzaldehyde	106.12	38.2
Isovaleraldehyde	86.13	42.5
Valeraldehyde	86.13	42.5
o-Tolualdehyde	120.15	36.9
m,p-Tolualdehyde	120.15	35.9
Hexanaldehyde	100.16	39.4
2,5-Dimethylbenzaldehyde	134.18	34

Source: SUPELCO DSD-DNPH Application Manual Revision 1.12B

Task 2: Quantification of Carbonyl Compounds in Bangkok in Urban Air

3.7 Determine the concentration level, spatial distribution, and diurnal distribution of carbonyl compounds in Bangkok

3.7.1 Sampling locations

Under this task, the researcher, collected ambient air samples from 11 sites, in which 9 sites were the Ambient Air Quality Monitoring Stations for Pollution Control

Department (PCD), while the other 2 sites which did not belong to PCD were Bangkok Naval Base as residential area and DonMuang District Office as roadside area. The sites were classified as roadside areas, residential areas. For the roadside area 5 sites were selected namely: DonMuang District Office (RO1), Transportation Department (RO2), Dindang Station (RO3), Chokchai Police Station (RO4), and Bannongbon School (RO5). For the residential areas, 5 sites were also selected namely: Bangkapi Sukhumnawaphan School (RS1), Bodindecha School (RS2), Watsingh School (RS3), Bangkok Naval Base (RS4), Prachanukul School (RS5). The map of the 10 sampling sites is shown in Figure 3.17. And the details of each sampling site is shown in Table 3.10. The picture of each sampling site is shown in Appendix D

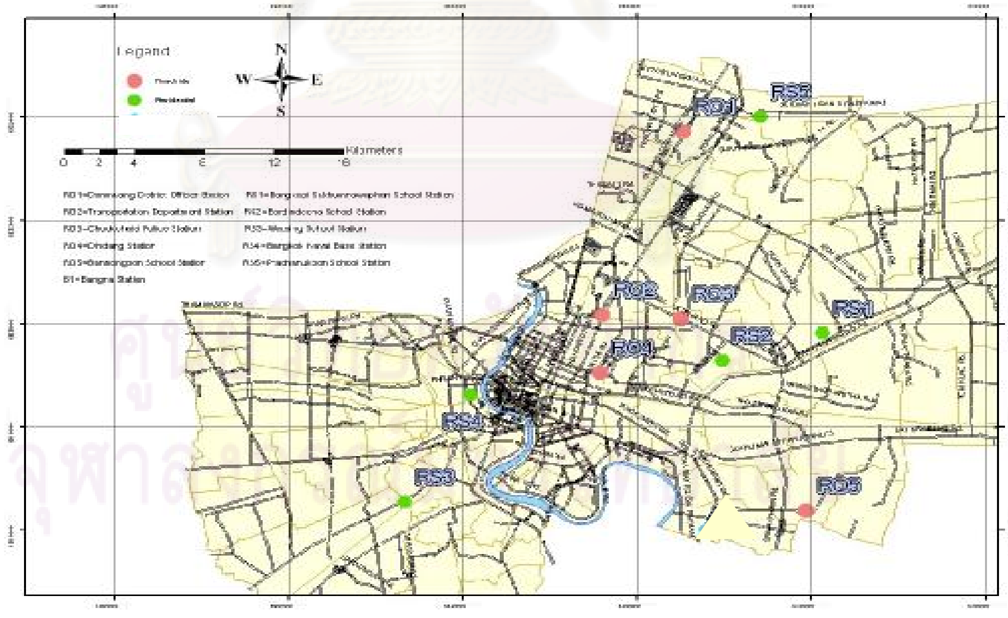


Figure 3.17 Map of Bangkok showing the 10 sampling sites

Table 3.12 Detail description and GPS information of the 10 sampling sites.

No.	Stations	UTM Coordinate		Nearest Meteorological Station	Remarks
		X (WGS8)	Y (WGS8)		
Roadside areas					
RO1	DonMuang District Office	672318	1538355	Bangkok University Air Quality Monitoring Station	The population in Donmuang district is about 157,989 people. This sampling site is situated near Vipawadee road and toll-way. Opposite side of the sampling site is an old international airport of Thailand and domestic airport. The traffic density of DonMuang District is moderate approximately 1,576 vehicles/hr. Most of the vehicles are motorcycles.

RO2	Transportation Department	667714	1525914	Transportation Air Quality Monitoring Station (PCD)	This sampling site is located at Jatujak district. The traffic density of the road is approximately 16,961 vehicles/hr. Opposite side is surrounded by open market selling various kinds of goods. There are many passenger buses passing this road.
RO3	Chokchai 4 Police Station	672180	1525636	Chokchai 4 Air Quality Monitoring Station (PCD)	The traffic density of the road is approximately 5,106 vehicles/hr. There are high-rise residential buildings close to the sampling site.
RO4	Dindaeng Station	667609	1522005	Dindaeng Air Quality Monitoring Station (PCD)	The sampling site is adjacent to Dindaeng road with high traffic density at approximately 6,838 vehicles/hr. The residential buildings are close to the site.

RO5	Bannongbon School	679577	1512599	-	The sampling site is located near Srinakarin road with high traffic density about 5,455 cars/hr. The site was set up at the 2nd floor of Bannhongbon School.
No.	Stations	UTM Coordinate		Nearest Meteorological Station	Remarks
		X (WGS8)	Y (WGS8)		
Residential areas					
RS1	Bangkapi Sukhumnawaphan School	680340	1524712	Klongjun Air Quality Monitoring Station (PCD)	This site is situated at Bangkapi Sukhumnawaphan School. About 500 meter radius are low-rise and high-rise residential buildings and one car garage.
RS2	Bodin Decha School	674557	1522832	Ramkhmheang Air Quality Monitoring Station (PCD)	About 500 meter radius, there are schools, residential building, mobile meat grills, two car garages and one furniture factory.

RS3	WatSingh School	656372	1513271	Watsing Air Quality Monitoring Station (PCD)	The sampling site is close to a temple. About 500 meter radius, there is one temple, schools, residential buildings, mobile meat grills and one car garage
RS4	Bangkok Naval Base	660128	1520475	Bansomdet Air Quality Monitoring Station (PCD)	The sampling site was set up at the open landscape. The height of the sampling shelter was about 1.5 meters, and surrounded with grass field and pond.
RS5	Prachanukul School	676790	1539354	-	About 500 meters radius, there are densely populated residential villages, small shops, mobile meat grills and one car garage.

3.7.2 Sampling Technique

The sampling technique employed under this task was DNPH active cartridge sampler. The appearance of DNPH active cartridge sampler is shown in Figure 3.8. This sampling technique has its advantage because a large volume of ambient air can be precisely collected by using a pump, which in turn makes sufficient amount of target substances available for accurate quantitative analysis. The sampling system consisted of a battery powered pump (Sibata mini pump MP E30, Japan) that draws the ambient air into the sampling cartridge under a flow rate of 0.100 liters per minute. An ozone scrubber was attached in front of the active cartridge to trap ozone interference that can react with the DNPH and cause negative biases. The sampling system was also provided with a heater (GASTEC, GTH-1, Japan) to prevent moisture to enter the cartridge and may cause effect to the real concentration of carbonyl compounds under study. The sampling system was placed in a shelter to prevent direct sunlight, rain, and strong winds to the collecting system. Figure 3.8 shows the DNPH active sampling for carbonyl compounds.

3.7.3 Determine the concentration of carbonyl compounds in Bangkok urban area.

Samples were collected using DNPH active cartridges at 10 sites in Bangkok, to determine the concentration level of carbonyl compounds in roadside and residential areas during July 2007 to April 2008. Ambient air were collected for 24 hours in every site. Fifteen carbonyl compounds were measured in Bangkok ambient air namely: formaldehyde, acetaldehyde, acetone, acrolein, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexanaldehyde, and 2,5-dimethylbenzaldehyde. The peaks of m-tolualdehyde and p-tolualdehyde cound not be separated, therefore the concentration was reported as m,p-tolualdehyde. There were about 150 samples collected during this period. The samples were extracted and analyzed by HPLC using UV detector. Statistical evaluation of the data were done by using the t-test calculations.

3.7.4 Determination of daily concentration variation in roadside and residential areas in Bangkok.

Under this task, samples were collected daily for 7 days in 2 roadside areas (DonMuang and Chokchai 4) and 1 residential area (Prachanukul School), by using DNPH-active sampling technique. There were about 60 samples collected during May 2008 to August 2008. The samples were extracted and analyzed by HPLC using UV detector. Under this task, the concentration ratio of formaldehyde to acetaldehyde were also determined.

3.7.5 Diurnal measurement of carbonyl compounds in roadside area in Bangkok.

Ambient air samples were collected every 3 hours in Don Muang roadside area during August 2008 by using DNPH active sampler. There were 30 samples collected for this measurement. Another set of samples were also collected at the same site for daytime and night time. There were 40 samples collected for this analysis.

3.8 Quality assurance and quality control

3.8.1 Sampling

Quality assurance and quality control was applied during sampling such as:

- Duplicate sampling – this was done during collection of samples at 11 sites to determine the monthly concentration of carbonyl compounds, which was done by collecting 2 samples at 1 site for roadside area and 2 samples at I site in residential areas. The criteria was that the concentration difference of these 2 samples collected at the same site should not exceed 20% difference.
- Field Blanks- 3 blank cartridge were brought to the sampling site every time sampling was done. These 3 blank cartridge were opened at the site but not exposed during the following day (collection of samples). Then they are resealed and brought back to the laboratories for extraction and analysis. The criteria for field blanks was that the concentration of carbonyls present in each cartridge should not higher than the detection limit (0.03 mg/l) for each compound.
- Sampling sites- each sampling site represented the specific area of study in which roadside areas were located near the roadside with heavy traffic density, while the residential areas were located away from main roads and industries but lies within the area where most people build houses. However, many schools were also built within these residential areas therefore, most of the samples were allocated in schools.

-Transportation and storage of samples- all samples collected were resealed in a Teflon bag stored in ice box during transport to the laboratory, and kept at -86 °C freezer before extraction.

3.8.2 Analysis

-Extraction of samples- all samples should be extracted immediately upon arrival to the laboratory. However, in cases where extraction could not be possibly done immediately, the samples should be tightly sealed and stored in -86 °C freezer before extraction. Extraction must be done within 1 day after collection.

-Reagent blank analysis- all reagents such as distilled water and solvent used during extraction and analysis must be HPLC grade. The newly purchased reagents and chemicals should be injected to the HPLC prior to use, in order to determine the contamination level of carbonyl compounds in each lot of chemicals. These reagents and solvents should also be injected to the HPLC before performing any analysis. The concentration of carbonyl compounds present in each reagent and chemicals should not exceed the detection limit for every carbonyl compound.

-Laboratory blank analysis- at least 3 blank cartridge should be analyzed for laboratory blanks before any analysis of carbonyl compounds.

-Calibration curve- at least 5 points calibration curve should be prepared for every month. However, if some changes was made in the

HPLC system, such as replacement of parts, columns, guard columns, seals and frits were done, or a repair of the instrument was done, a new calibration curve must be constructed again. A new IDL and IQL must also be done.

- Daily calibration curve- a daily calibration curve should also be done everyday to check the stability of the HPLC instrument. The concentration of the daily calibration is 0.1 mg/l which is the middle concentration of the real calibration curve. The concentration difference of the daily calibration and the real calibration curve should not exceed 10% difference.

- Check the retention of the daily calibration curve- Aside from checking the concentration of carbonyl compounds, the retention of each compound should also be evaluated every analysis. The percent deviation of retention time for each carbonyl compound in every sample must be within 0.05 minutes from the real calibration curve.

-Avoid contamination of glassware and other materials - all materials used such as volumetric flaks, syringes, septum, vials, test tubes, pipette tips, inserts, vial caps, should be first washed with distilled water and finally washed with acetonitrile HPLC grade, then dried in oven for 3 hours, and cool in a dessicator, packed in a Teflon bag, ready for use.

-The researcher- during sampling and analysis of carbonyl compounds, the researcher must not use any perfume or cosmetics, and should not drink any alcoholic drinks too, in order to prevent contamination from personal source.

3.9 Calculation of the Concentration of Carbonyls in the Samples.

$$\mu g/m^3 = \frac{\mu g\ \text{concentration from analysis} - \text{blank}\ \times (\text{final volume})}{\text{sampling rate (L/min)} \times \text{sampling time (min)}} \times 1000$$

Task 3.

3.10 Determine the Traffic Volume in Roadside Areas

Under this task, the researcher used the video camera attached to a computer to record the traffic flow at roadside areas, Chokchai 4 which has a high traffic density, DonMuang which has medium traffic density. Recording was done at these sites during May to July 2008. The concentration of carbonyl compounds were also measured at these sites during these periods by collecting samples using active samplers. The concentration of carbonyl compounds were plotted together with the number of vehicles that flow at those areas. Although all types of vehicles were recorded the researcher calculated only the cars and motorcycles because these types of vehicles used gasohol as fuel for their engines. Figure 3.19 shows the CCTV camera used for recording the traffic density.

Figure 3.18 Video Camera recorder to record traffic density in the roadside areas.

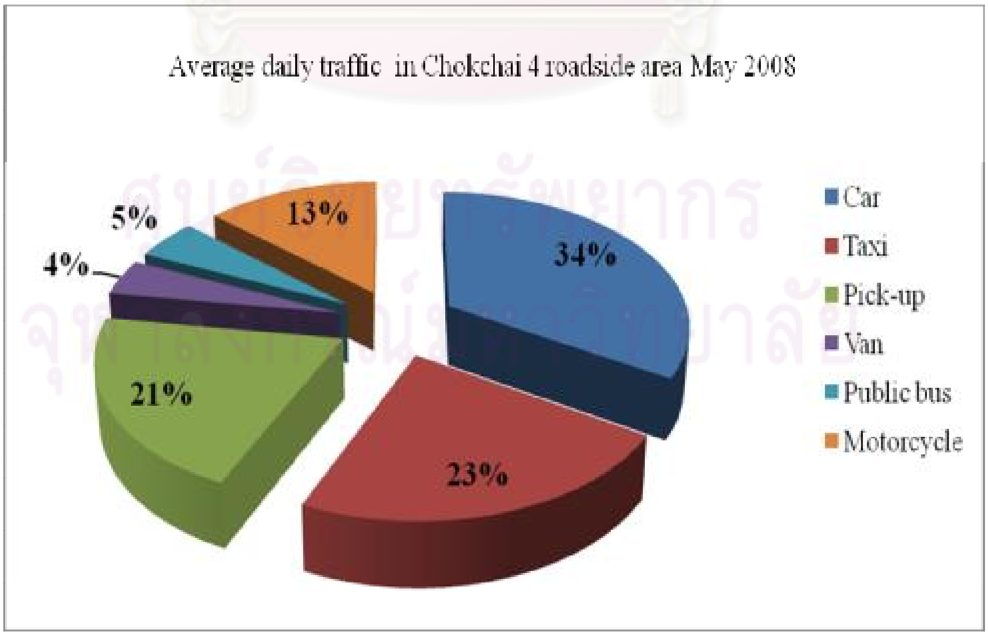


Figure 3.19 Average daily traffic density in Chokchai 4

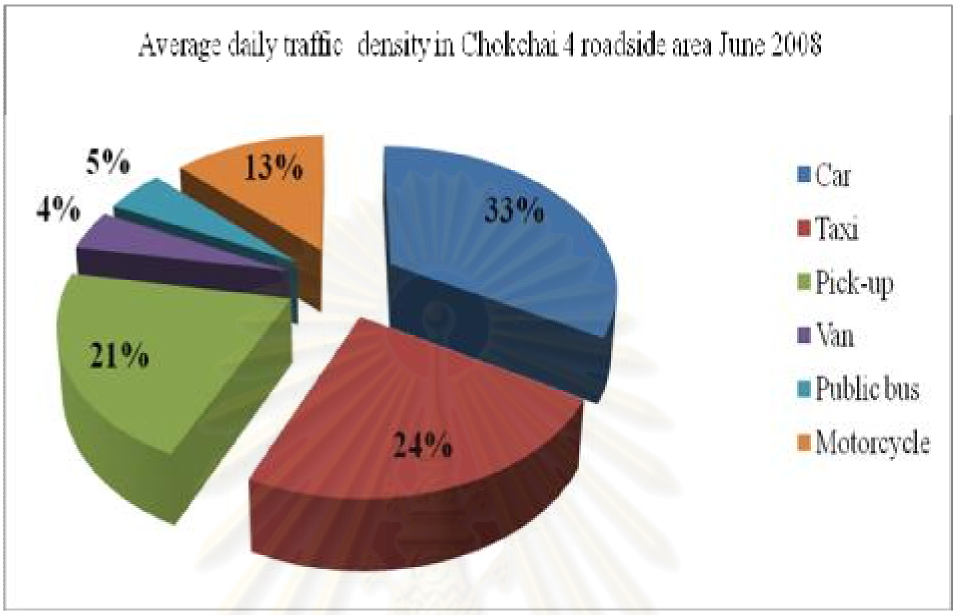


Figure 3.20 Average daily traffic density in Chokchai 4

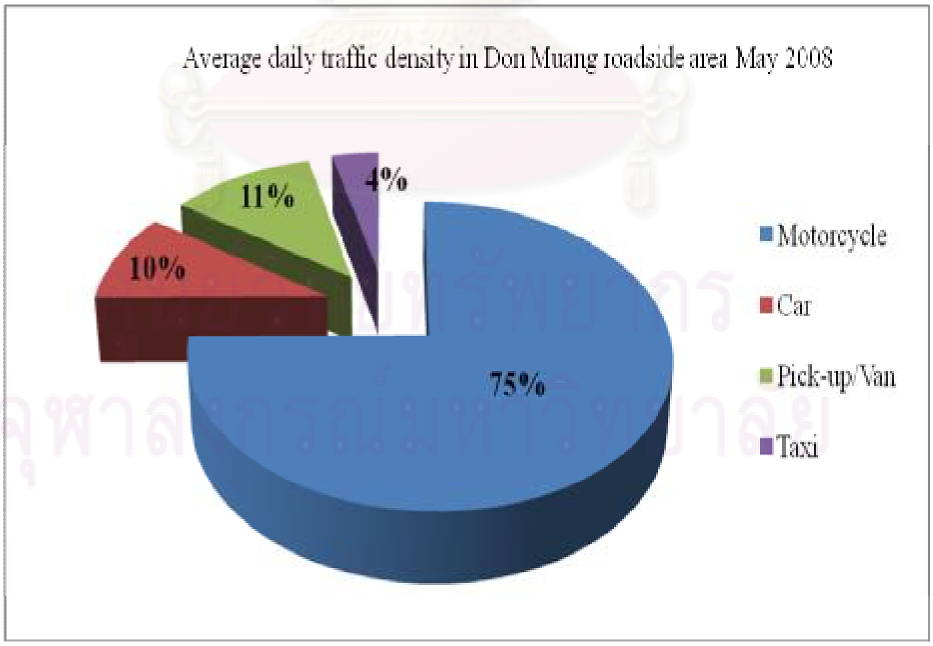


Figure 3.21 Average daily traffic density in Don Muang

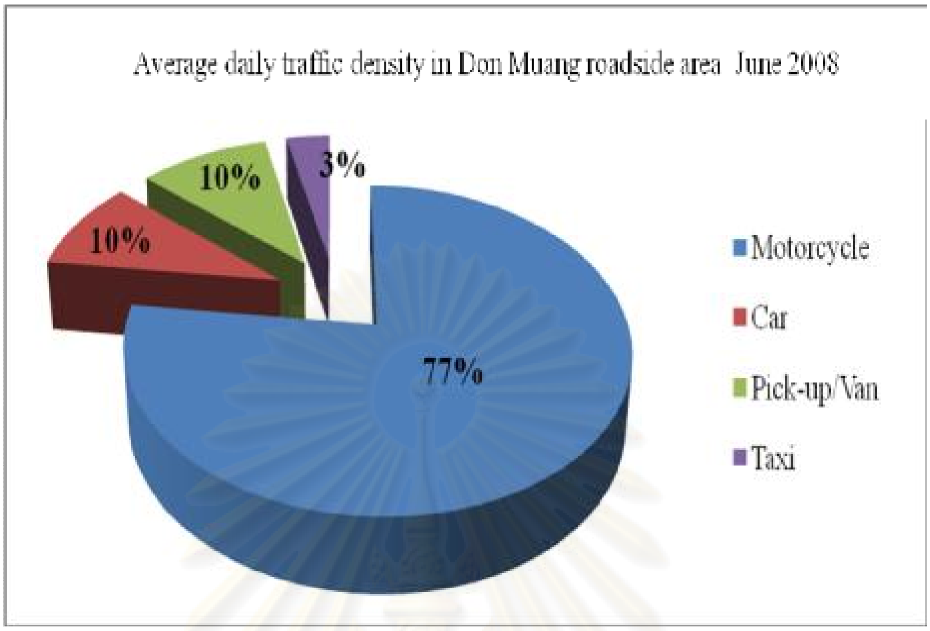


Figure 3.22 Average daily traffic density in Don Muang

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Preliminary Survey for Carbonyl Compounds in Bangkok

On March 2006, a preliminary investigation for carbonyl compounds was done at 49 sites in Bangkok. Ambient air were collected for 24 hours using DNPH passive sampler. The map of the sampling site for preliminary study is shown in Figure 3.13. Carbonyl compounds were measured and results showed that 10 carbonyl compounds were present in Bangkok ambient air. The analysis also revealed that formaldehyde was found in all the 49 sampling sites, acetaldehyde was found in 36 sampling sites, acetone was found in 34 sites, benzaldehyde was found in 26 sites, propionaldehyde was found in 24 sites, butyraldehyde was found in 18 sites, valeraldehyde was found in 13 sites, acrolein was found in 12 sites, crotonaldehyde was found in 11 sites and isovaleraldehyde was found in 4 sites. The number of sites showing presence of carbonyl is shown in Figure 4.1. Other compounds were not detected. The concentration of formaldehyde ranged from 0.20-10.5 $\mu g/m^3$ while, the concentration of acetaldehyde ranged from ND-2.92$\mu g/m^3$, the concentration of acetone ranged from ND-1.25$\mu g/m^3$, the concentration of benzaldehyde ranged from ND-0.62 $\mu g/m^3$, the concentration of propionaldehyde ranged from ND – 0.33 $\mu g/m^3$, the concentration of butyraldehyde ranged from ND- 0.33$\mu g/m^3$, the concentration of valeraldehyde ranged from ND-0.95$\mu g/m^3$ the concentration of acrolein ranged from ND-1.45$\mu g/m^3$, and, the concentration of, the concentration of crotonaldehyde ranged from ND-0.49$\mu g/m^3$ and the concentration of isovaleraldehyde ranged from ND- 0.70$\mu g/m^3$. High concentration of formaldehyde was found from sample collected near Huaykwang market, Victory monument, Suthisan road, Rachadapisek road, and Rama V. High concentration of acetaldehyde was found from sample collected at Sukumvit 33. Huaykwang and Suthisan and Victory monument. The high concentration of formaldehyde in Rama V may come from vehicles and another source such as formalin because the samples were collected near the Rama hospital and Ratchavithi hospitals. Acetaldehyde concentration was high in Sukumvit due to vehicles and other sources such as building painting or outdoor cooking. The result of the survey also showed that about 31 sites exceeded the formaldehyde cancer unit risk of 1 ppbv given by OEHHA and about 16 sites exceeded the acetaldehyde cancer unit risk of 1 pbbv given by the OEHHA. Since nearly all the 49 samples were collected near the roadside area, it can be said that the source of emission of these carbonyl compounds were emitted mostly from the transportation sector. Figure 4.2 shows the concentration of formaldehyde in Bangkok during March 2006, while Figure 4.3 shows the concentration of acetaldehyde in Bangkok during March 2006.

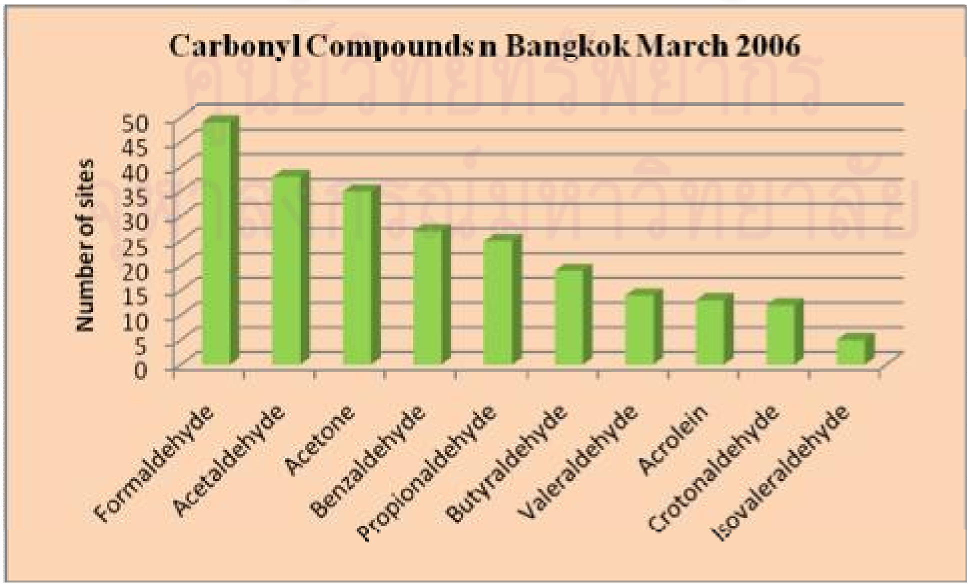


Figure 4.1 Prevalent carbonyl compounds in Bangkok ambient air

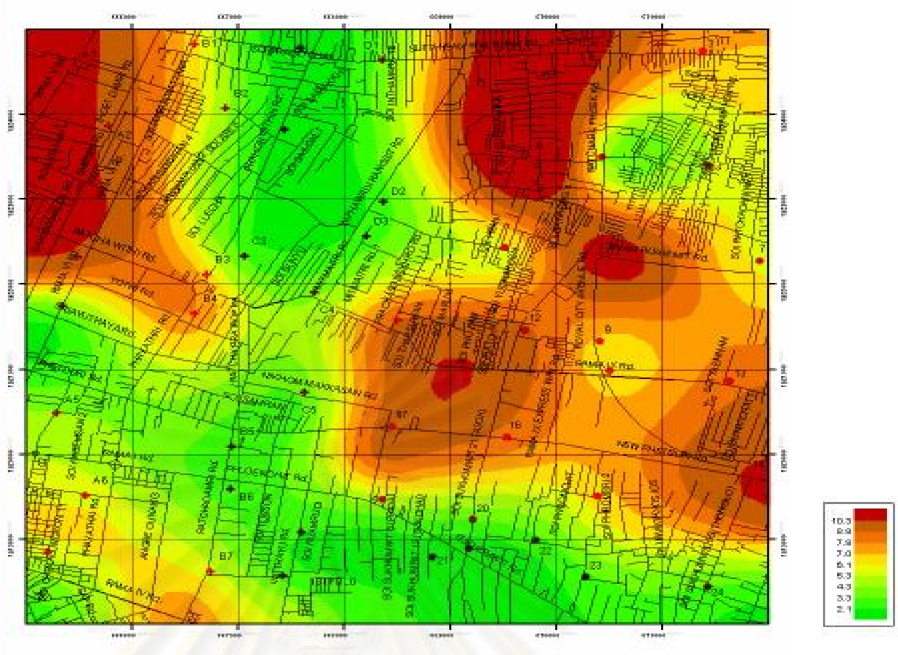


Figure 4. 2 Contour map for Formaldehyde concentration on March 2006

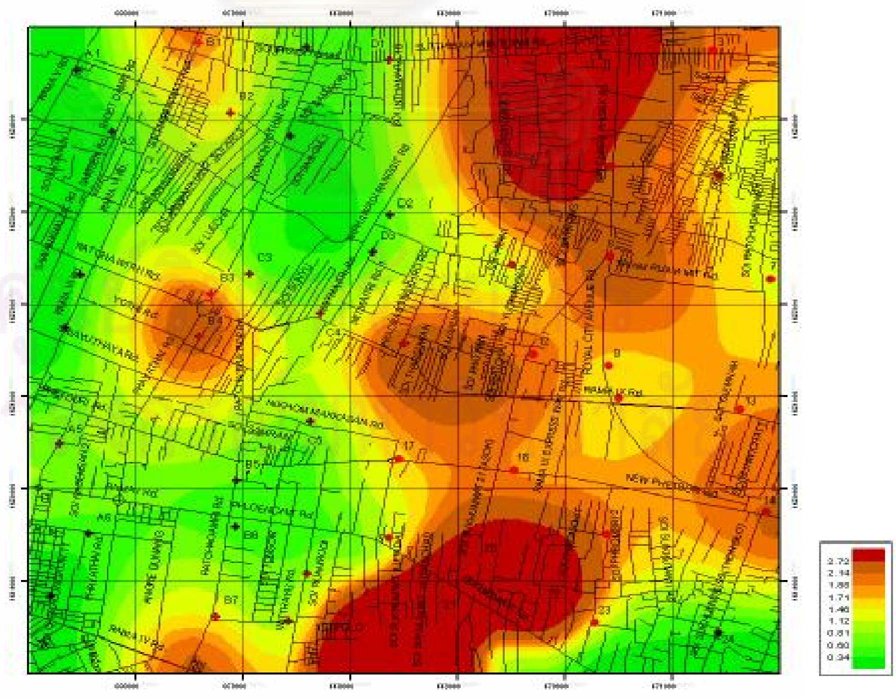


Figure 4.3 Contour map for Acetaldehyde concentration on March 2006

4.2. Concentration Level of Carbonyl Compounds in Bangkok.

To determine the concentration level of carbonyl compounds in roadside and residential areas in Bangkok, samples were collected at 10 sites by using DNPH-active. samplers. The sampling duration was 24 hours. Fifteen carbonyl compounds were measured in the ambient air samples namely: formaldehyde, acetaldehyde, acetone, acrolein, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexanaldehyde, and 2,5-dimethylbenzaldehyde. The prevalent carbonyl compounds found in Bangkok were formaldehyde, acetaldehyde, acetone, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, and hexanaldehyde.. The most abundant carbonyl compound found in roadside areas and residential areas was formaldehyde which constituted about 35% of all the carbonyls, acetone ranked the second which constituted about 30%. Many of the sources of acetone involve the oxidation of higher molecular weight hydrocarbons, but the relative contribution of primary, non anthropogenic, sources, e.g., biogenic and oceanic, may be significant. It is also emitted from industrial processes, solvents, paints, and tobacco smoke, biomass burning, terrestrial vegetation, plant decay, and the oxidation of isoalkanes, monoterpenes, and methylbutenol The mean tropospheric lifetime of acetone is estimated to be 15 days (Graedel, T. E. et al., 1986). Acetaldehyde ranked the third which constituted only about 11%, other carbonyls showed low concentrations. as seen in Figure 4.4. Other carbonyl compounds such as pripionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, valeraldehdye, isovaleraldehdye, and hexanaldehyde showed very low percent contribution to carbonyl compounds in Bangkok's urban air. Although these compounds are also emitted from the transportation sector, they are also emitted from other sources such as industrial emissions, tobacco smoke, cooking, organic chemicals, paints, solvents, etc.

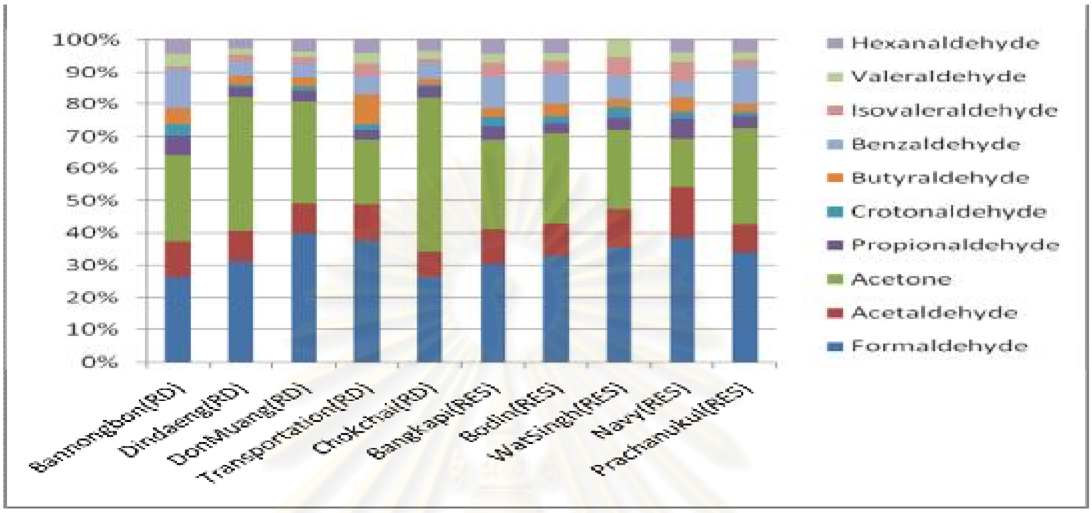


Figure 4.4 Percentage of carbonyl compounds in 10 sampling areas in Bangkok

The ambient concentration of formaldehyde at the roadside areas in Bangkok during July 2007 to April 2008 ranged from 5.14 to 17.2 $\mu g/m^3$ (average 11.53 $\mu g/m^3$) while, the ambient concentration of formaldehyde in residential areas in Bangkok during the same period ranged from 3.06 to 19.9 $\mu g/m^3$ (average 9.65 $\mu g/m^3$). The concentration of acetaldehyde in roadside areas in Bangkok during July 2007 to April 2008 ranged from 1.59 to 7.95 $\mu g/m^3$ (average 3.51 $\mu g/m^3$) while at the residential areas the concentration of acetaldehyde during the same period ranged from 1.07 to 8.05 $\mu g/m^3$ (average 3.11 $\mu g/m^3$). Other compounds showed low concentration. The concentration of carbonyl compounds in DonMuang (RO1), Transportation (RO2), Dindaeng (RO3), Chokchai 4 (RO4), and Bannongbon (RO5), are shown in Figure 4.5, Figure 4.6, Figure 4.7, Figure 4.8, and Figure 4.9 respectively. The concentration of carbonyl compounds in Bangkapi School (RS1), Bodin Decha School (RS2), Wat Singh (RS3), Bangkok Naval Base (RS4), and Prachanukul School (RS5), are shown in Figure

4.10, Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14, respectively. It was also found that the concentration level of formaldehyde and acetaldehyde in the roadside areas are higher due to emissions from cars and motorcycles that use gasohol as fuel. The concentration of formaldehyde in the residential areas may be transported from the roadside areas and photochemical reaction.

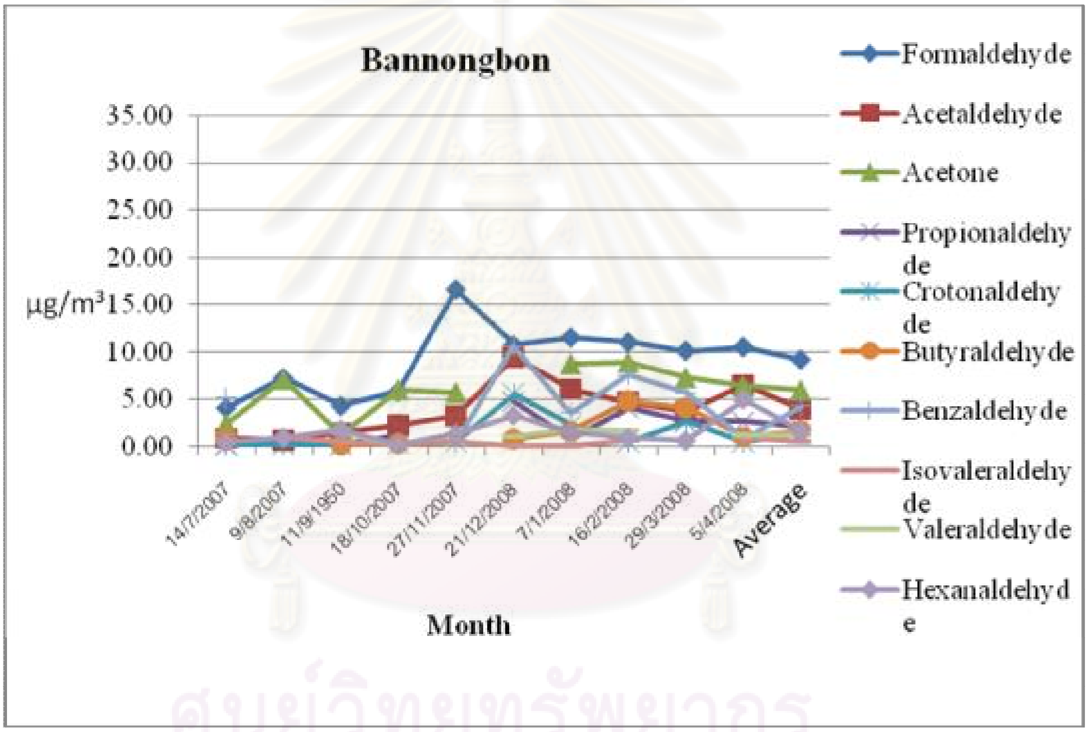


Figure 4.5 Concentration of carbonyl compounds in Bannongbon during July 2007-April 2008

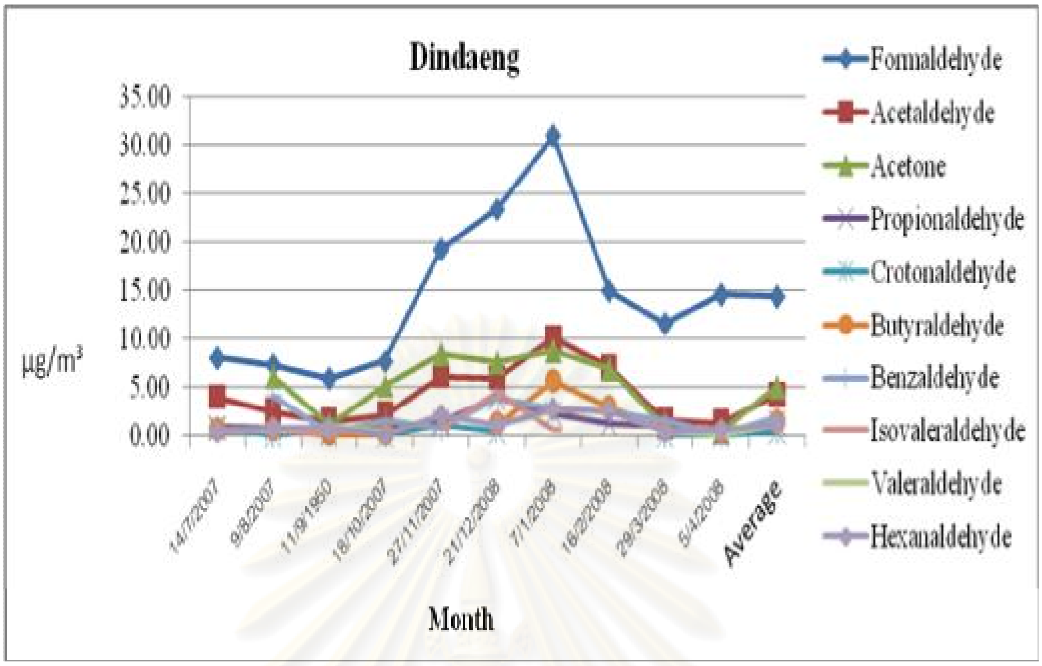


Figure 4.6 Concentration of carbonyl compounds in Dindaeng during July 2007 - April 2008.

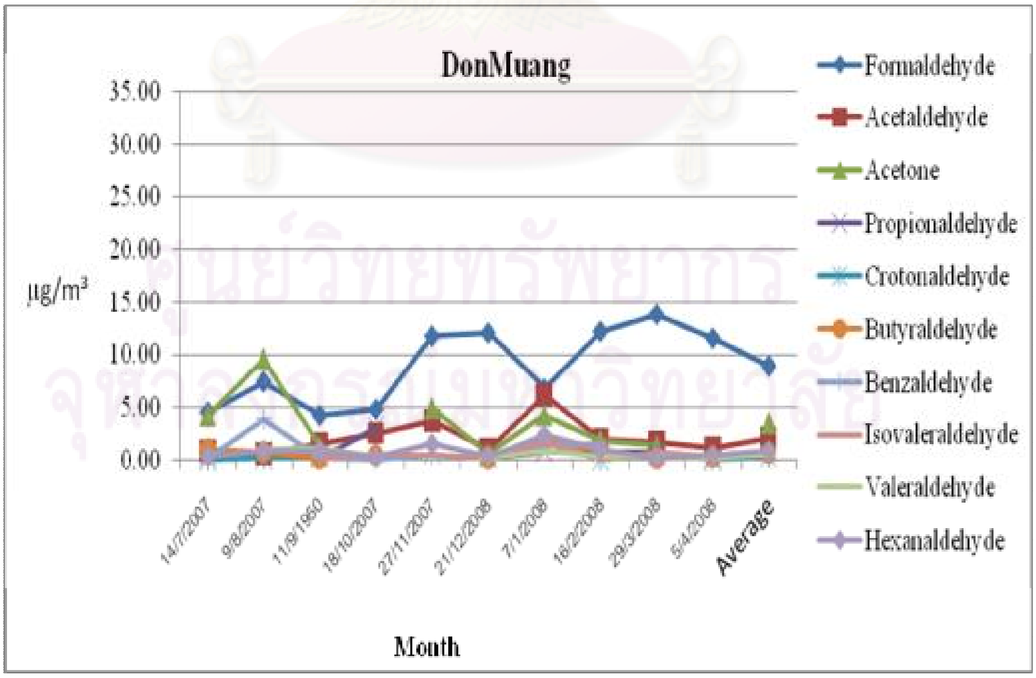


Figure 4.7 Concentration of carbonyl compounds in DonMuang during July 2007-April 2008

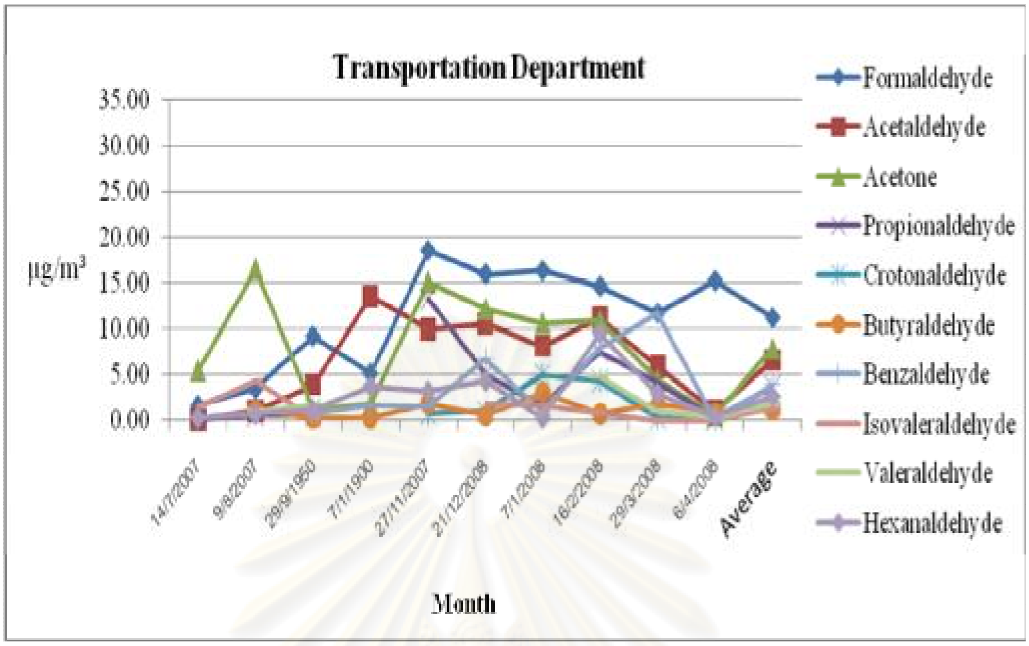


Figure 4.8 Concentration of carbonyl compounds in Transportation Department during July 2007-April 2008.

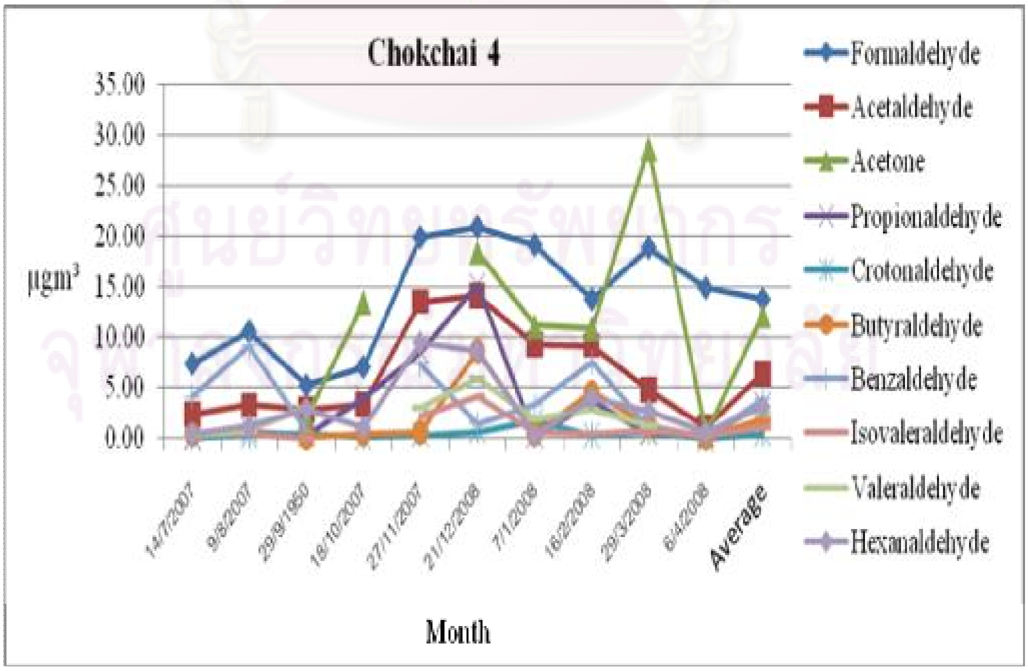


Figure 4.9 Concentration of carbonyl compounds in Chokchai 4 during July 2007- April 2008

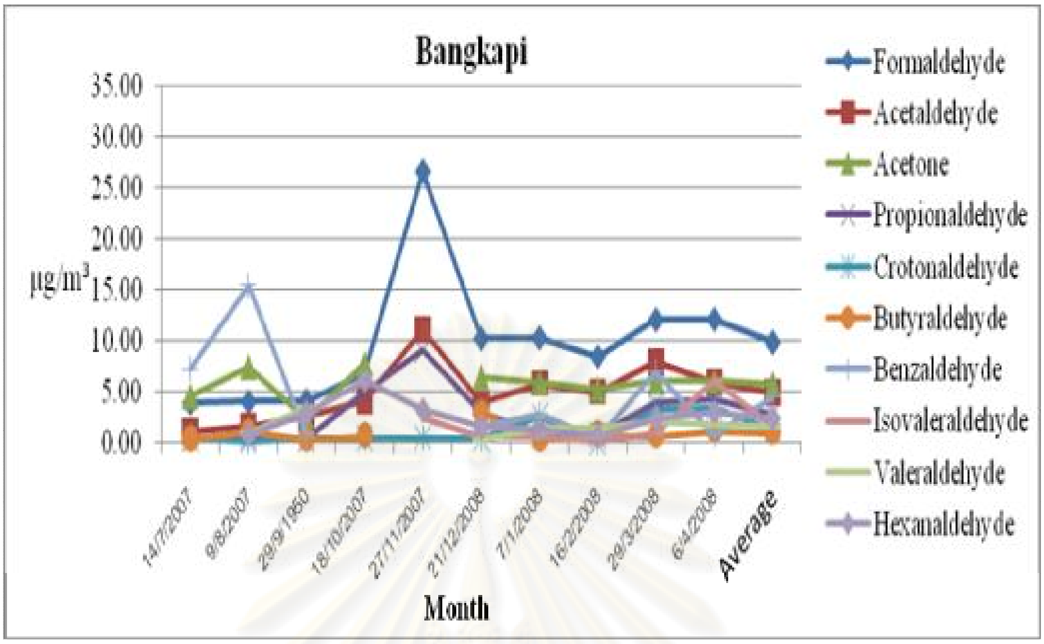


Figure 4.10 Concentration of carbonyl compounds in Bangkapi during July 2007-April 2008

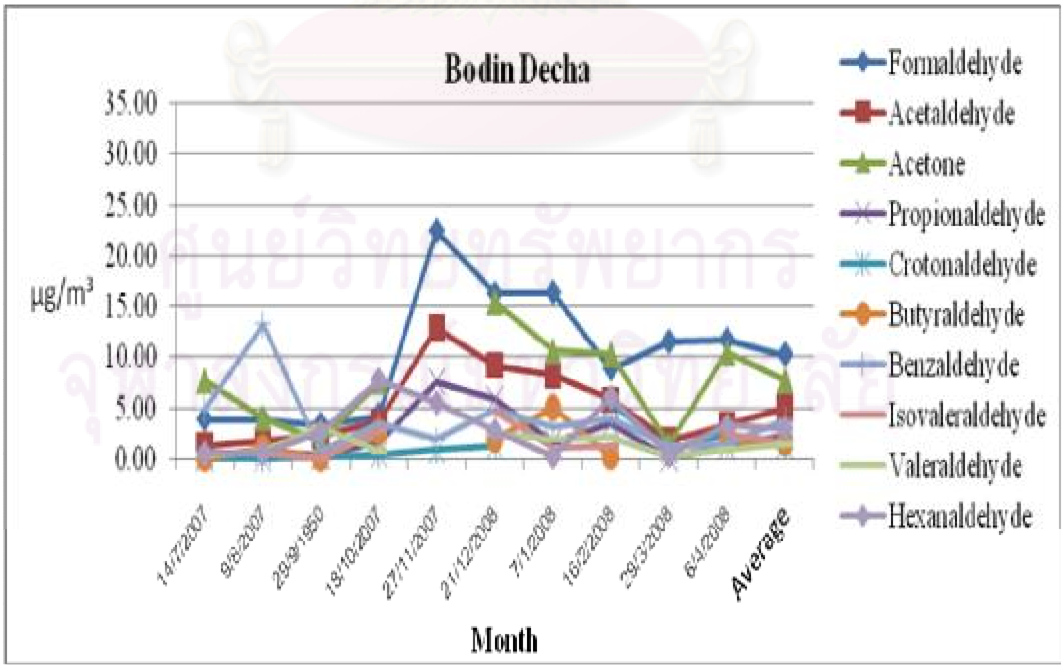


Figure 4.11 Concentration of carbonyl compounds in Bodin Decha during July 2007-April 2008

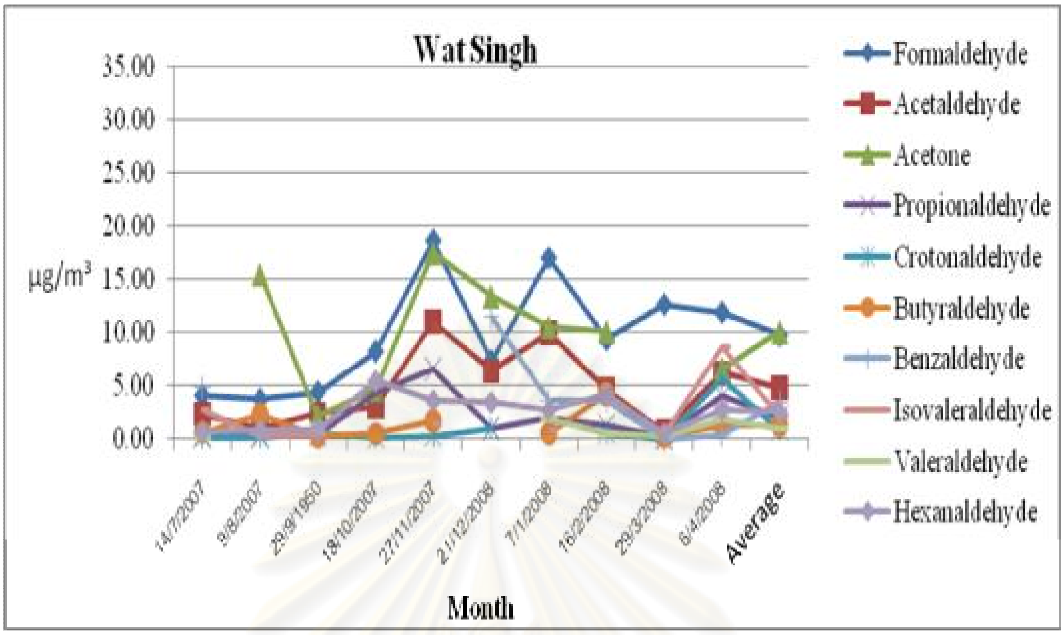


Figure 4.12 Concentration of carbonyl compounds in Wat Singh during July 2007-April 2008.

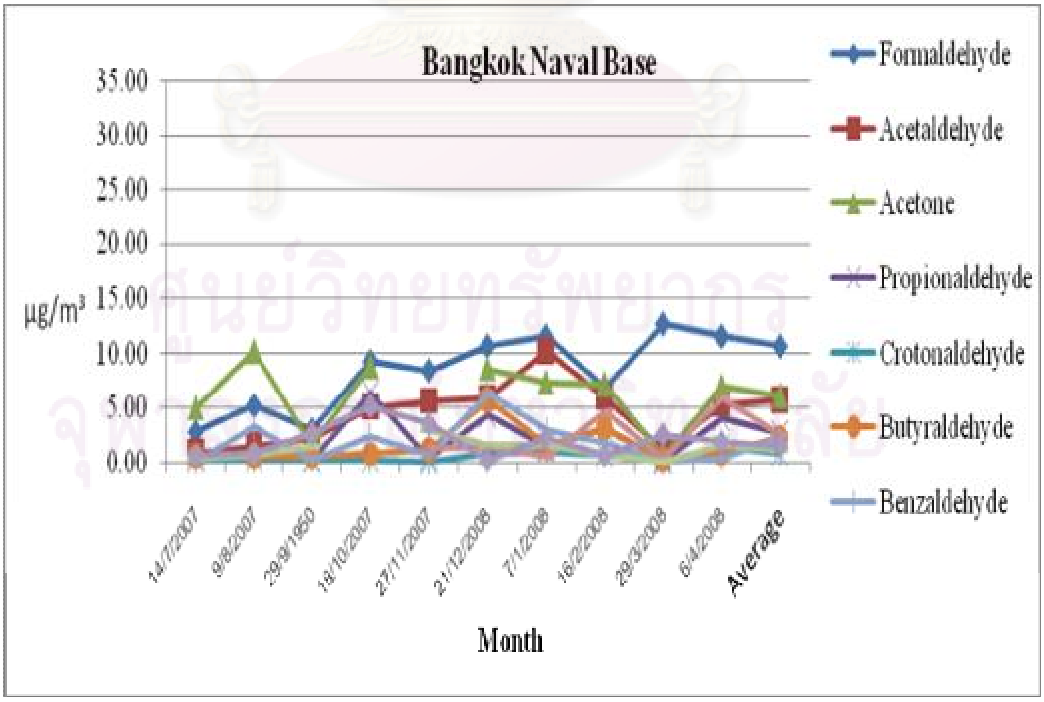


Figure 4.13 Concentration of carbonyl compounds in Bangkok Naval Base during July 2007-April 2008.

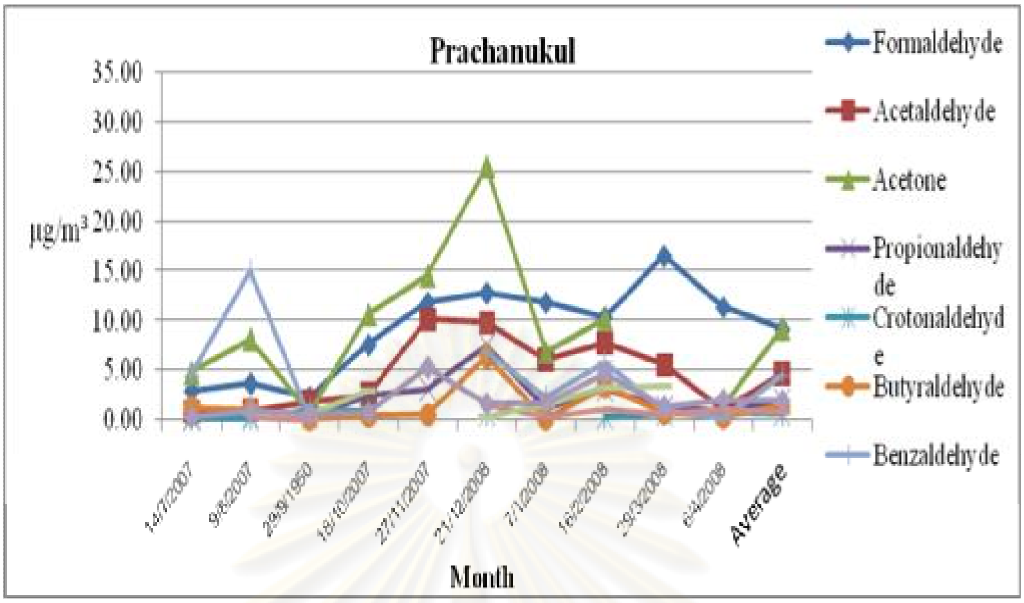


Figure 4.14 Concentration of carbonyl compounds in Prachanukul on July 2007-April 2008

As can be noticed from all the graphs that the concentration of formaldehyde, acetaldehyde, and acetone were low during the month of July and September 2007. This result can be explained from the meteorological condition in Bangkok that during July and September 2007 the amount of rainfall was 270mm and 260mm respectively and in DonMuang which is 255mm and 286mm respectively as shown in Table 3.1. During the month of August, formaldehyde and acetaldehyde concentration increased due to lower rainfall amount. During October 2007 until April 2008 the weather was dry. These findings can explain that wet deposition can significantly affect the concentration of carbonyl compounds. Although these compounds are water soluble they do not possess treat to under groundwater because they are biodegradable compounds.

Generally, the oxidation of ethanol which is contained in the gasohol fuel would yield acetaldehyde. But in this study, it was revealed that the most abundant carbonyl found in Bangkok was formaldehyde. In this case, photo-oxidation of acetaldehyde occurred in the atmosphere such as reaction with hydroxyl radicals as stated by (Atkinson and Lloyd, 1984; Atkinson et al., 1989,1990), that products formed from photo-oxidation of acetaldehyde include peroxyacetyl nitrate and formaldehyde. On the other hand, photolysis of acetaldehyde produces methyl radical that react with oxygen to form methyl peroxyl radical, which reacts with nitric oxide to form formaldehyde (Horowitz and Calvert, CARB,1993).

4.3 Seasonal variation of carbonyl compounds in Bangkok

It can also be seen from Figure 4.16, that the concentration of formaldehyde and acetaldehyde were high in the roadside areas which explains that the source come from vehicle emissions especially cars and motorcycles that use gasohol, due to rapid increase in gasohol consumption, that caused increased concentration of these compounds in Bangkok ambient air. The concentration of formaldehyde and acetaldehyde in the residential areas were lower due to absence of direct sources. Therefore, photo-oxidation and photolysis of acetaldehyde plays an important contribution in the formation of formaldehyde in the residential areas in Bangkok. Although, transport of these pollutants from the roadside areas can not be denied.

It is remarkably noted that the concentration of carbonyl compounds exhibit seasonal fluctuations as seen in Figure 4. 15. The concentration of formaldehyde and acetaldehyde were low during the rainy season (July –October) which is due to rain washout because these compounds are water soluble. As stated by (Tanner R.L. et al., 1988) that heterogeneous losses by wet deposition processes are significant especially formaldehyde due to its high aqueous solubility. Washout ratios (concentration in rain/concentration in air) are 28 and 37 which were estimated by Atkinson, 1989 and Buttery et al., 1969, respectively. The concentration becomes high during the cold season (November to February) not only due to absence of rain, that enhance high concentration but also higher atmospheric reactivity that occurs during winter season that increases NOx concentration which favors photo-chemical production of formaldehyde. The concentration of formaldehyde and acetaldehyde slightly decrease during the summer season (March-June) which is due effect of high temperature strong sunlight, and humidity during the summer season wherein, these compounds are volatile organic compounds, so their concentrations are affected by these environmental factors. Other photochemical reactions may also occur such as photolysis of acetaldehyde due to high temperature produces methyl radical that can react with oxygen to form methyl peroxyl radical, which reacts with NOx to form formaldehyde. Consequently, these compounds may also react with NOx in the presence of strong sunlight to produce ozone, thereby reducing their ambient concentrations. The seasonal variation of formaldehyde and acetaldehyde in Bangkok is shown in Figure 4.16.

The difference in acetaldehyde residence time varies between season. The summer residence time are short in most cases, whereas the winter residence time are on the order of days. The winter residence time for formaldehyde is easier to asses. For acetaldehyde calculation of winter residence time is difficult due to importance of secondary formation. The major uncertainty in the residence time calculation for acetaldehyde is the OH radical concentration, which varies from day to day by a factor of two (Mackay et al., 1995). According to studies conducted by (CARB, 1993), revealed that in Los Angeles, direct emissions are important sources of formaldehyde and acetaldehyde in ambient air during winter time or night time.

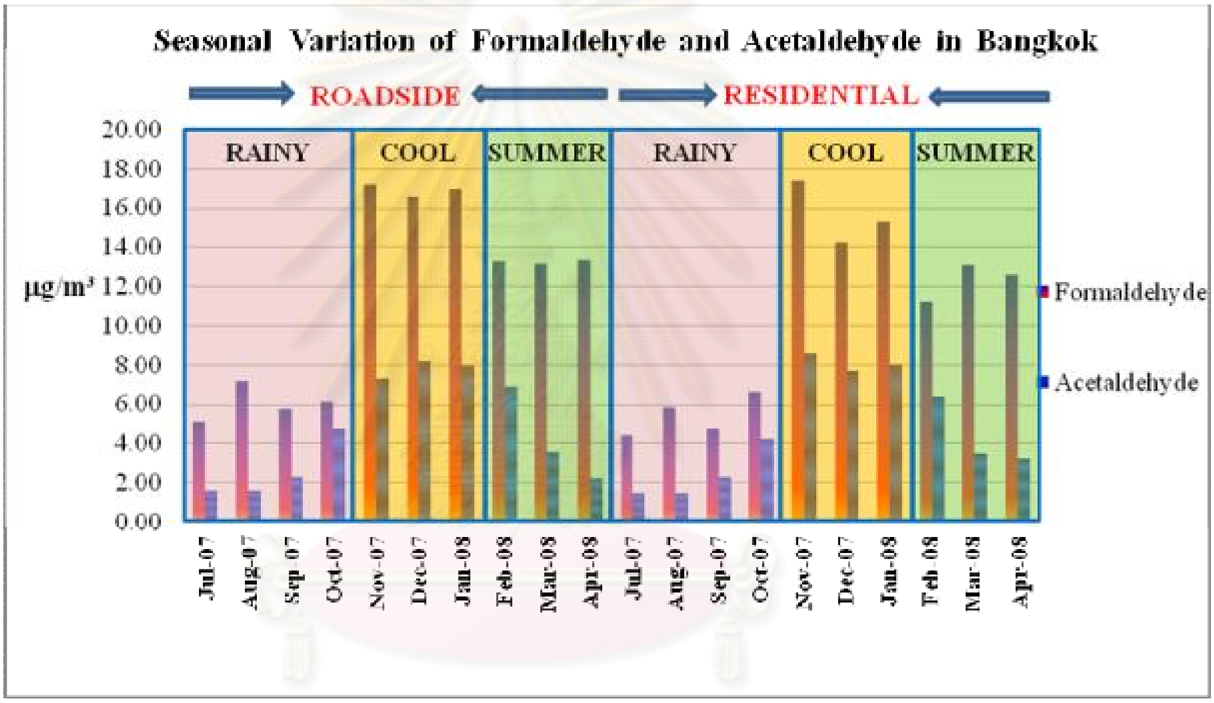


Figure 4.15 Seasonal Variation of formaldehyde and acetaldehyde in Bangkok

4.4 Daily concentration of formaldehyde and acetaldehyde in Bangkok in relation to traffic density.

While formaldehyde and acetaldehyde are not a composition in the gasohol fuel, but rather a product of incomplete combustion from vehicles fuelled with gasohol. All internal combustion have the potential to produce these compounds. However, the concentration of the pollutants generated depends primarily on the composition of the fuel, the type of engine, the emission control system, the operating temperature, the age, and the inspection and maintenance of the vehicle. Therefore, the concentration of these compounds in ambient air maybe variable.

The Pollution Control Department project on “Measurement of Toxic Air Pollutants from Gasohol Fuelled Cars” reported that by using gasohol as fuel, benzene and 1,3 butadiene concentration will decrease at 12.86% and 55.71% respectively. While other toxic air pollutants such as ethyl benzene, acetaldehyde and formaldehyde will increase at 122.34%, 127.27%, and 20.72% respectively. These tests were performed directly at the exhaust pipes of cars and motorcycles that use gasohol and gasoline as fuel. Based on the results of their test, it can be expected that the rates of release of acetaldehyde from cars and motorcycles using gasohol will increase. The increase consumption of gasohol could result in increase emission of acetaldehyde.

At present, gasoline 91 is still used as fuel in some cars and motorcycles in Thailand. The gasoline 91 did not contain ethanol but use MTBE (11% volume) as the octane booster. Most studies found that MTBE increases formaldehyde emissions (Hood and Farina, 1995). Therefore, using both gasoline 91 and gasohol as fuel, the concentration of formaldehyde in ambient air at Bangkok is expected to be high.

In order to assess the daily variation in the concentration of formaldehyde and acetaldehyde in ambient air in relation to car and motorcycles density, measurement was conducted at Chokchai 4 and DonMuang during May to June 2008. In Chokchai 4, cars constituted about 34%, and motorcycles constituted about 14% of the total traffic density, while in DonMuang motorcycles constitute about 70% and cars constitute only about 10% of the total traffic density. The cars and motorcycles density was summed and plotted with the concentration of formaldehyde and acetaldehyde. Figure 4.17, and Figure 4.19 show the concentration of formaldehyde and acetaldehyde in Chokchai 4 during May and June 2008. The results indicated good relationship between the concentration of formaldehyde and acetaldehyde with the volume of cars and motorcycles in this sampling area. On the other hand, the concentration of formaldehyde and acetaldehyde was also compared to the total volume of car density which included all types of vehicles. The results indicated unsatisfactory results, thereby indicated that other types of vehicles did not contribute to the concentration of formaldehyde and acetaldehyde in Chokchai 4 as shown in Figure 4.18 and Figure 4.20. Another set of air samples and volume of traffic density was collected in DonMuang during the same period with Chokchai 4. Figure 4.21 and Figure 4.23 showed the concentration of formaldehyde and acetaldehyde in DonMuang during May and June 2008. The results indicated good relationship between the concentration of formaldehyde and acetaldehyde and the amount of cars and motorcycles in this sampling area. On the other hand, the concentration of formaldehyde and acetaldehyde was also compared to the total volume of car density which included all types of vehicles. The results indicated unsatisfactory results, thereby indicated that other types of vehicles did not contribute to the concentration of formaldehyde and acetaldehyde in DonMuang as shown in Figure 4.22 and Figure 4.24.

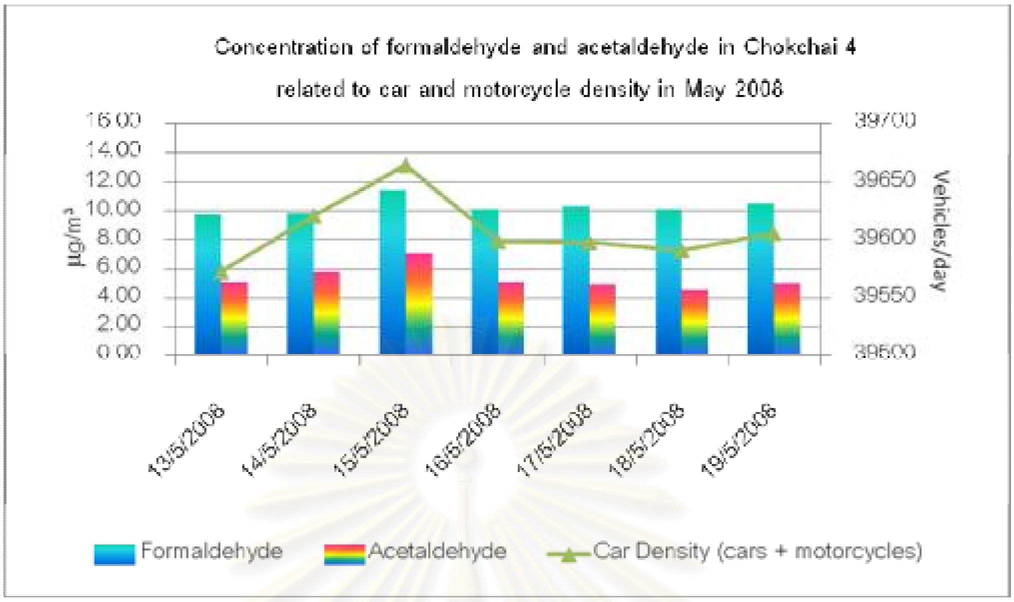


Figure 4.16 Concentration of formaldehyde and acetaldehyde in relation to car and motorcycle density in Chokchai 4 on May 2008.

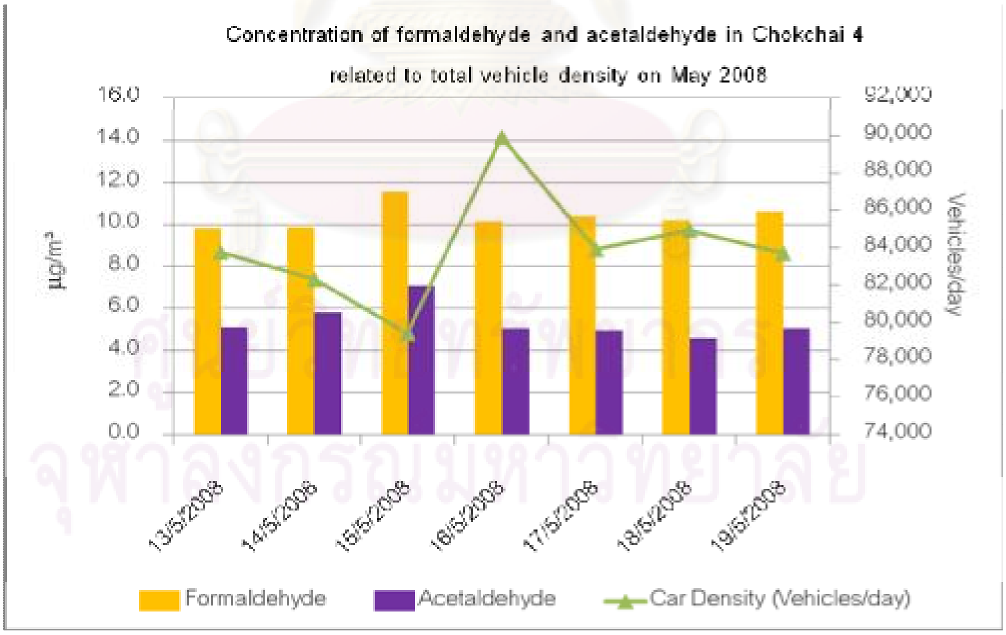


Figure 4.17 Concentration of formaldehyde and acetaldehyde in relation to total traffic density in Chokchai 4 on May 2008.

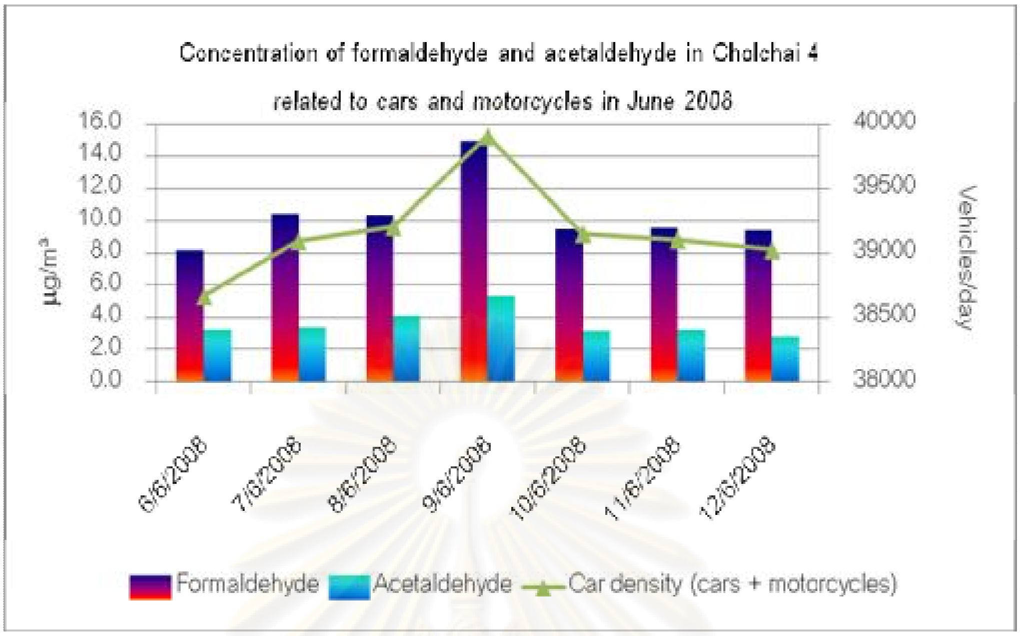


Figure 4.18 Concentration of formaldehyde and acetaldehyde in relation to Car and motorcycle density in Chokchai 4 on June 2008.

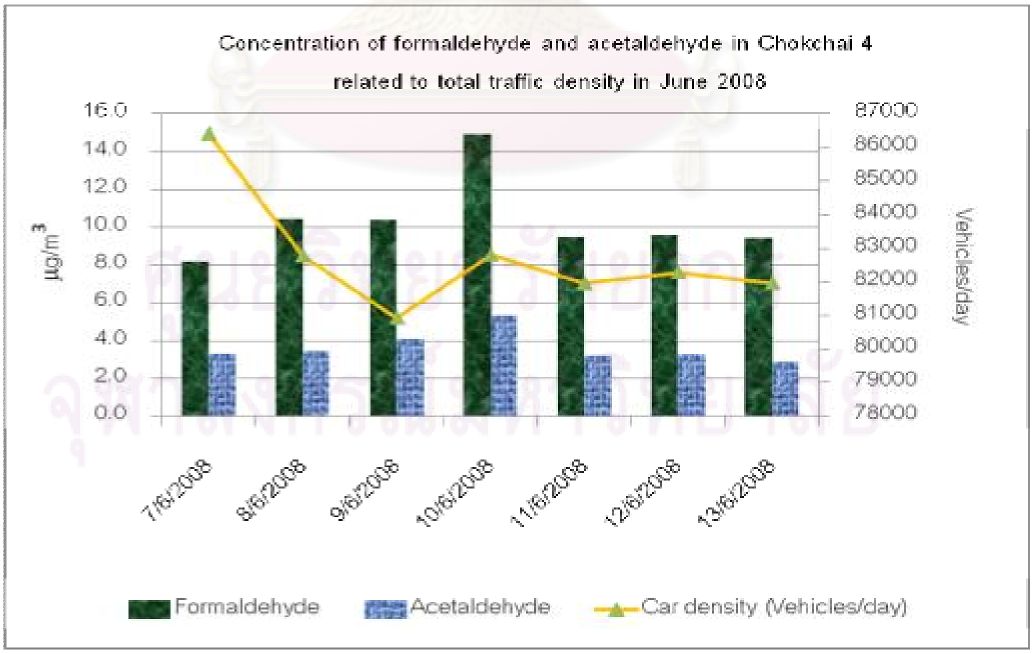


Figure 4.19 Concentration of formaldehyde and acetaldehyde in relation to total traffic density in Chokchai 4 on June 2008.

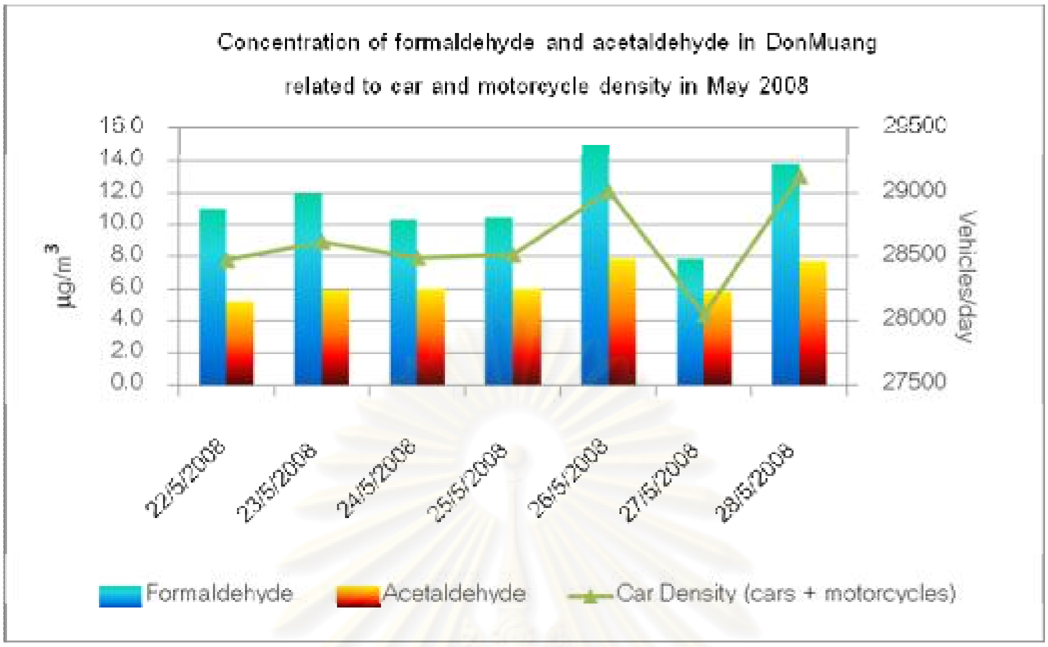


Figure 4.20 Concentration of formaldehyde and acetaldehyde in relation to car and motorcycle density in Don Muang on May 2008.

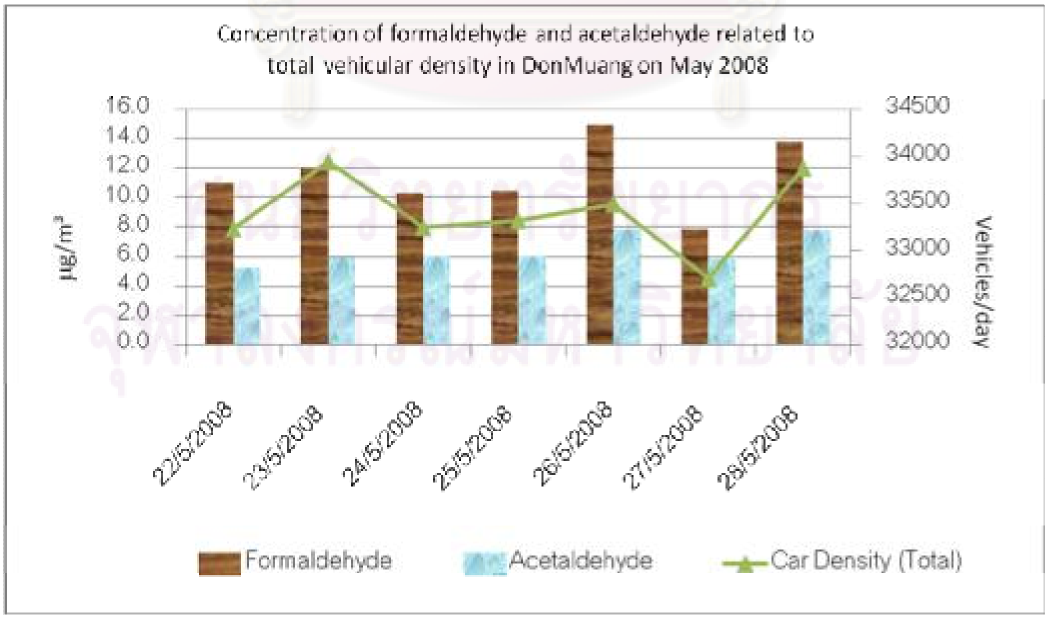


Figure 4.21 Concentration of formaldehyde and acetaldehyde in relation to total traffic density in Don Muang on May 2008.

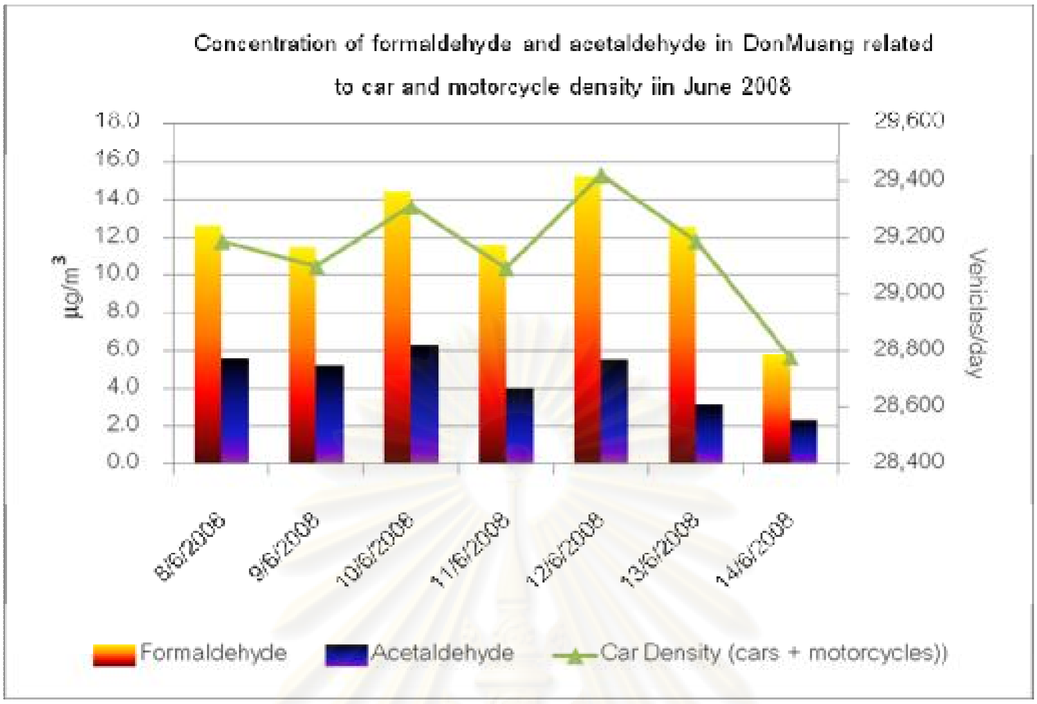


Figure 4.22 Concentration of formaldehyde and acetaldehyde in relation to car and motorcycle density in Don Muang on June 2008.

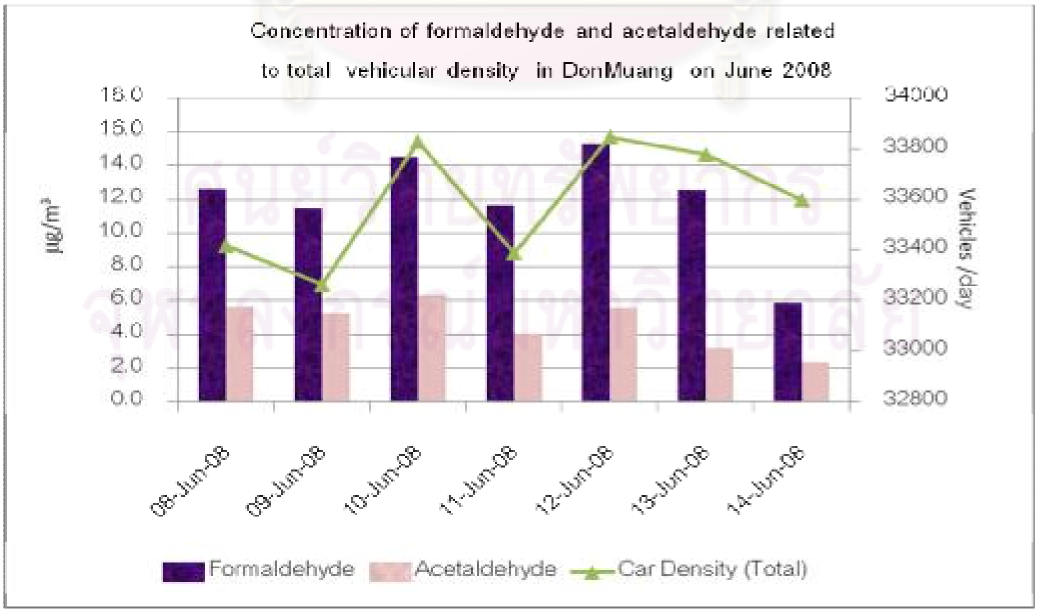


Figure 4.23 Concentration of formaldehyde and acetaldehyde in relation to total traffic density in Don Muang on June 2008.

In order to evaluate the hourly concentration of formaldehyde and acetaldehyde related to hourly traffic density, another measurement of carbonyl compounds were collected for every 3 hours at Don Muang during June 2008. The results showed during 5:00 A.M. to 8:00 A.M, the concentration of formaldehyde significantly increased which was related to the increase in sources such as solar radiation and traffic density. During 9:00 A.M. to 14:00 P.M. the traffic density decreased but the concentration of formaldehyde and acetaldehyde still remain high due to photochemical reactions. During 17:00 to 20:00 P.M, traffic density increase, and the concentration of these two compounds were still high. However, from 20:00 P.M. to 05:00 A.M. the concentration of formaldehyde and acetaldehyde rapidly decrease due to absence of solar radiation that enhance photochemical reaction, so cars and motorcycles that use gasohol are the only sources of formaldehyde and acetaldehyde during those hours as seen in Figure 4.24.

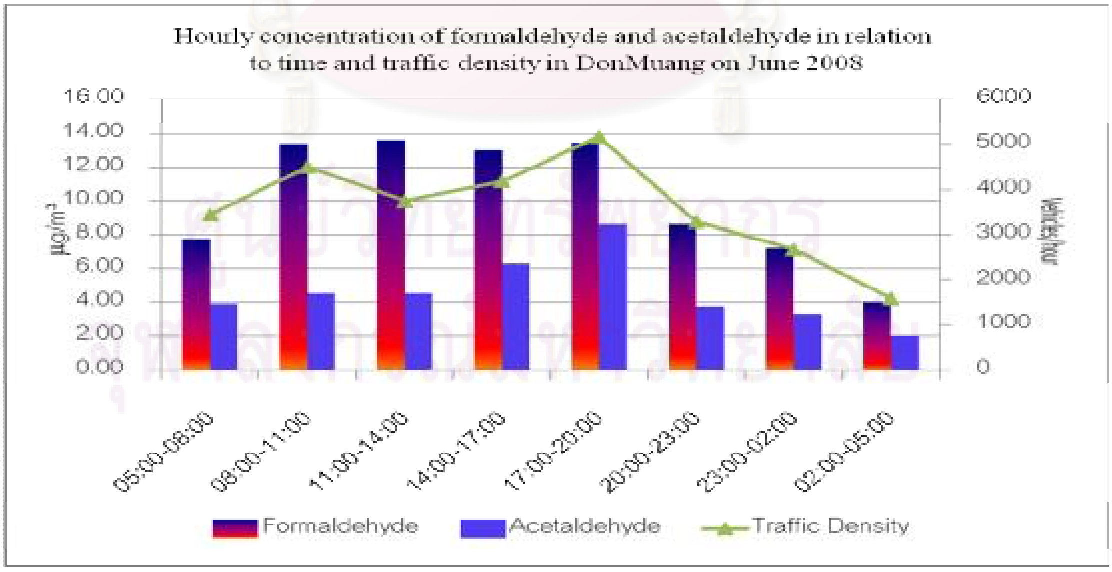


Figure 4.24 Hourly concentration of formaldehyde and acetaldehyde related traffic density

4.5 Correlation of carbonyl compounds with car density in Bangkok

The correlations between formaldehyde and acetaldehyde at DonMuang roadside area were also measured by collecting ambient air samples at different time periods. High correlations between formaldehyde and acetaldehyde (R=0.9571) were obtained especially during 17:00-05:00., as shown in Figure 4.25, which may explain that these two compounds were produced by vehicular emissions According to Possanzini et al., high correlations between most carbonyl compounds were found during 18:0 0-21:00 which was the time period with the lowest solar radiation and in turn least photochemical reactions making vehicular emissions the major source. He further explained that during the time periods 11:00-17:00, formaldehyde showed high concentrations due to vehicular exhaust as well as the reaction rates of both photochemical generation under high solar radiation in daytime were considered significant. Under this study, the results showed similar findings as Possanzini et al., 1996. Many studies revealed that the acetaldehyde is not a component of evaporative emissions but rather emitted in the exhaust of ethanol blended fuel and gasoline. The correlation of formaldehyde with car density was calculated to evaluate the car contribution to formaldehyde concentration levels in ambient air in Bangkok, as shown in Figure 4.26. From this figure we can see a very good correlation (R^2= 0.977) which can clearly show that formaldehyde are emitted from vehicles. Hence, it is expected that there is an increase emission of 0.0148 $\mu g/m^3$ formaldehyde from a car using gasohol which can be obtained from the slope of the graph. Likewise, the correlation of acetaldehyde with car density was also calculated to evaluate the car contribution to acetaldehyde concentration levels in ambient air in Bangkok, as shown in Figure 4.27. The results indicated that acetaldehyde concentration showed good correlation with car density (R^2= 0.926). Needless, to mention that the emission of acetaldehyde originated from vehicles. Hence, it is also expected that there is an increase emission of 0.0027 $\mu g/m^3$ acetaldehyde from a car using gasohol which can be obtained from the slope of the graph.

Gasohol fuel may lead to small decrease in carbon monoxide (CO) and nonmethane hydrocarbons (NMHCs). However, ethanol combustion in spark-ignition engines which will be cracked directly to acetaldehyde, particularly during cold starts of the vehicles, resulting in increased acetaldehyde and formaldehyde emissions. The reaction of acetaldehyde with OH radicals in urban atmosphere leads directly to the formation of peroxyacetyl radical, which can react with nitrogen dioxide (NO_2) to form formaldehyde. These compounds are known as human carcinogens. In cases where there is exposure to multiple carcinogens, the risk of each carcinogen is added. The assumption implicit in this is that the effect on cancer risk in the population exposed to multiple carcinogen is additive. It is possible that some carcinogen might be synergistic and some antagonistic.

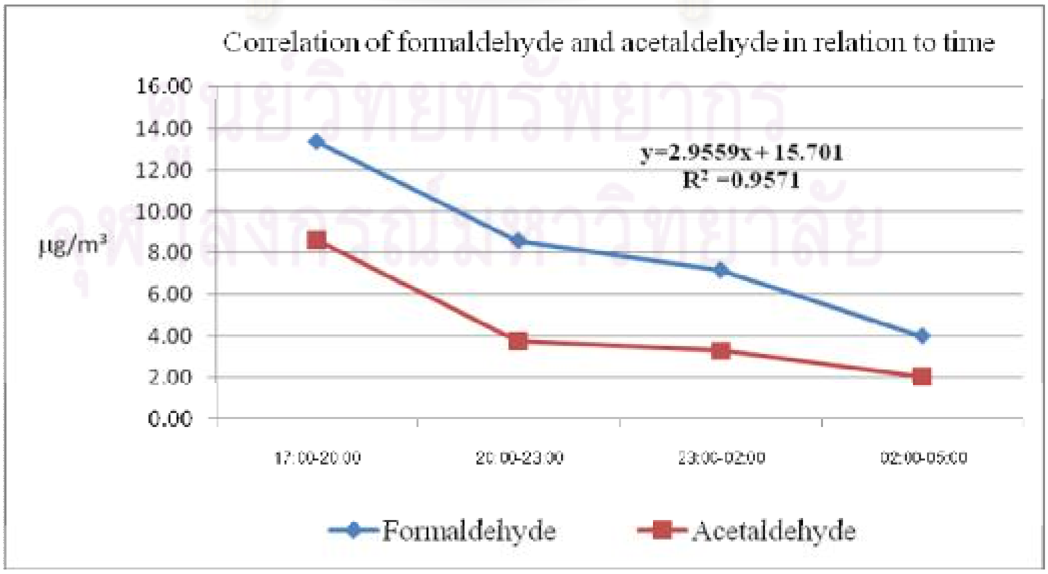


Figure 4.25 Correlation of formaldehyde and acetaldehyde in relation to time.

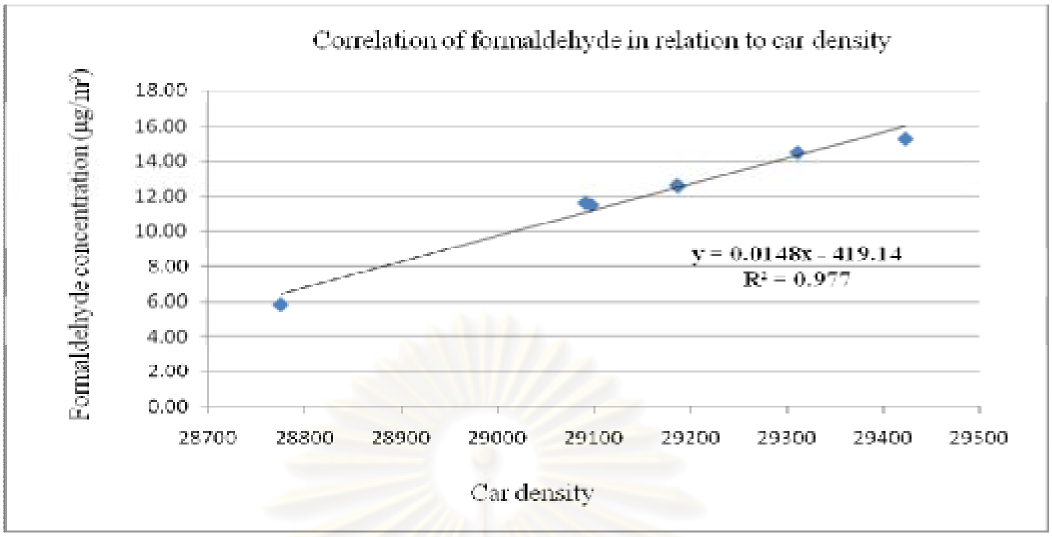


Figure 4.26 Correlation of formaldehyde in relation to car density

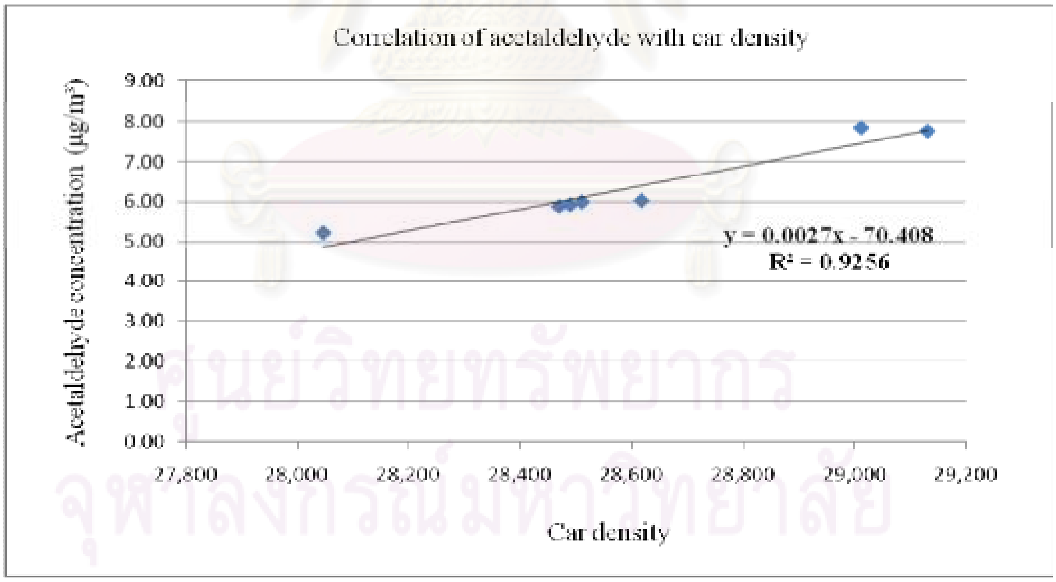


Figure 4.27 Correlation of acetaldehyde in relation to car density

4.6 Diurnal concentration of formaldehyde/acetaldehyde

. The concentration of formaldehyde and acetaldehyde were evaluated during daytime and nighttime at DonMuang and ERTC. It was found that the concentration of formaldehyde and acetaldehyde were higher in the daytime time as shown in Figure 4.29 and Figure 4.30. These findings coincides with Possanzini et al., 1996 explanations that formaldehyde showed high concentrations in the daytime due to vehicular exhaust as well as the reaction rates by photochemical generation under high solar radiation, while during night time period there was no solar radiation and in turn least photochemical reactions making vehicular emissions the major source.

During daytime, under clear sky conditions, the residence time of formaldehyde and acetaldehyde is determined primarily by their reaction with OH radicals, with photolysis accounting for a very negligible percent of removal (U.S. EPA, 1993). Factors influencing carbonyl compounds' atmospheric lifetime, such as time of day, sunlight intensity and temperature, also include those affecting the availability of hydroxyl radicals and nitrate radicals.

At night, the reaction of acetaldehyde with NOx will increase the production of formaldehyde (Atkinson et al., 1990). Due to high concentration of NOx in Bangkok, this reaction is expected to occur rapidly. However, mobile sources decrease during night time which can also result in lower concentration of formaldehyde and acetaldehyde.

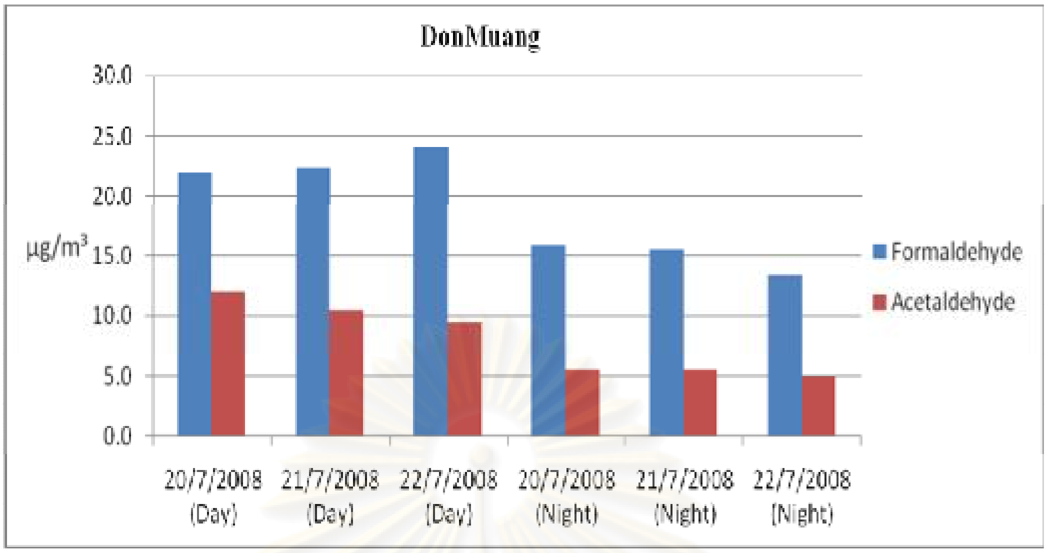


Figure 4.28 Daily concentration of formaldehyde and acetaldehyde in DonMuang during July 2008.

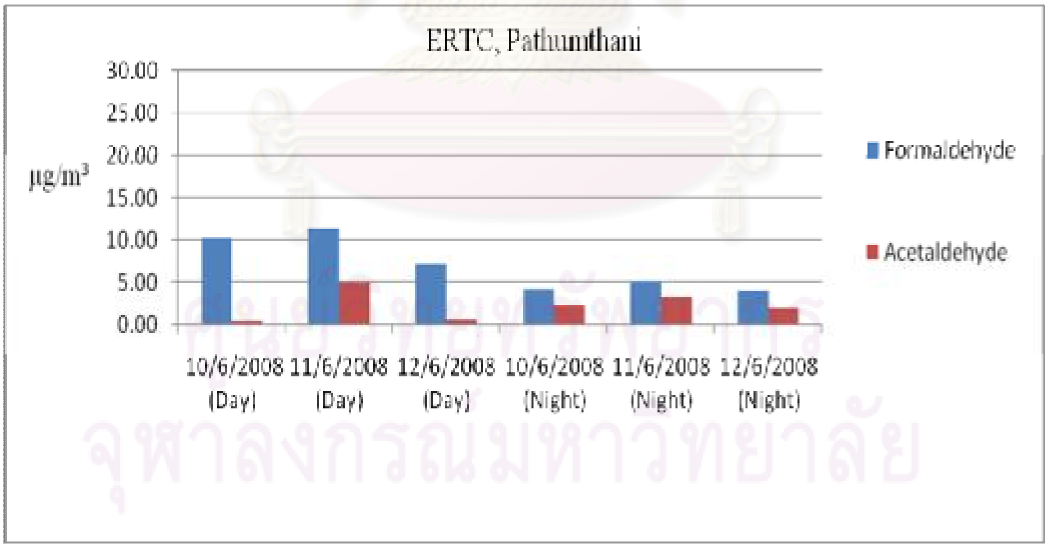


Figure 4.29 Daily concentration of formaldehyde and acetaldehyde in ERTC, Pathumthani during June 2008.

4.7 Comparison of concentration level of formaldehyde and acetaldehyde in Urban area, industrial area, and rural area.

Industrial releases of formaldehyde and acetaldehyde can occur at any stage during production, use, storage, transport or disposal of products with residual carbonyl compounds. Other transportation sources may also contribute to carbonyl compounds. To compare the concentration of carbonyl compounds in other areas in Thailand, samples were collected at the industrial area, rural area, and airport. Under this task, Chokchai 4 and DonMuang were selected to collect samples for Urban area. Mabthaput Industrial area was chosen to collect air samples for industrial area, and ERTC, Pathumthani, was selected to collect air samples for rural area. It was found that the concentration of formaldehyde and acetaldehyde were higher in Bangkok urban area (Chokchai 4 and DonMuang), than Mabthaput Industrial area, ERTC, Pathumthani, as shown in Figure 4.27. because the traffic density was very high in Bangkok compared the other areas. Moreover, formaldehyde and acetaldehyde were emitted from transportation sector. The result further indicated that the concentration of other carbonyl compounds such as acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, and hexanaldehyde were high in Mabthaput Industrial area, because these compounds comes from the industrial production processes. The concentration of formaldehyde and acetaldehyde in Mabthaput and ERTC, Pathumthani were similar due to low traffic density in those areas. This test gives an important explanation that transportation sector can contribute to high concentration of formaldehyde and acetaldehyde in ambient air, especially in highly congested traffic area like Bangkok.

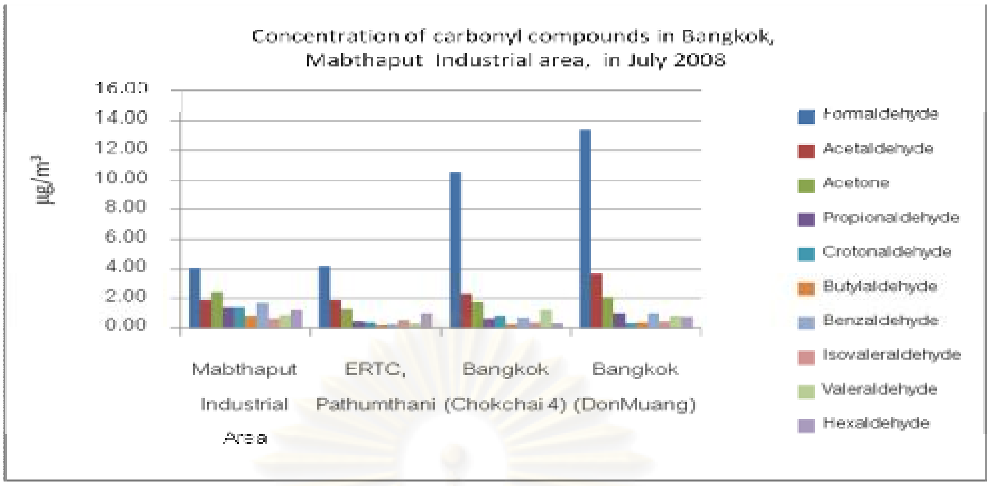


Figure 4.30 Average concentration of fcarbonyl compounds in Mabthaput Industrial area, ERTC –Pathumthani, Chokchai 4, and DonMuang on July 2008

4.8 Comparison of Carbonyl Compounds under this Study with Other Studies

The comparisons of the average concentrations of carbonyl compounds between this study and other countries that use gasohol was conducted. Brazil is the only country in the world that use gasohol up to 100% ethanol, although much of the light vehicles use 85% ethanol blended gasoline. It can be seen that the concentration of formaldehyde and acetaldehyde in Brazil was very high compared to other cities. The concentration of formaldehyde and acetaldehyde in Japan was lower than Brazil, Canada and this study, because Japan use only 3% ethanol blended gasoline in the industrial sector. In Canada, although they use 15% ethanol blended gasoline which have similar ratio as Thailand, the concentration of formaldehyde was lower, and the concentration of acetaldehyde was higher than Thailand. This is due to some factors, such as meteorological conditions, method of measurement, and preventive measures implemented to control the emission of carbonyl compounds in Canada. Table 4.1 shows the concentration of formaldehyde and acetaldehyde in different cities that use gasohol.

Table 4.1 Comparison of average concentrations of formaldehyde and acetaldehyde with other countries.

Aldehydes	(This study) μg/m³	Rio de Janeiro, Brazil (μg/m³)	Osaka, Japan (μg/m³)	Ontario, Canada (μg/m³)
Formaldehyde	10	67	2.3	3.9
Acetaldehyde	2.9	82	2.7	5.2
Fuel	E15	E100, E85	E3	E15

CHPATER V
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

Under this study, there were two major tasks carried out: (1) to quantify and evaluate the spatial and seasonal distribution of carbonyl compounds in Bangkok urban area and (2) to determine the concentration of carbonyl compounds in relation to traffic density.

5.1.1 Task 1: Quantify and evaluate the spatial distribution of carbonyl compounds in ambient in Bangkok

1) The concentration level of carbonyl compounds at the roadside and residential areas in Bangkok were high due to the high density of vehicles especially gasohol fuelled cars and motorcycles, which are the major sources of carbonyl compounds particularly formaldehyde and acetaldehyde. Therefore, increased use of gasohol will eventually result in high concentration of formaldehyde and acetaldehyde in ambient air in Thailand.

2) The concentration of carbonyl compounds in ambient air vary according to season, which is influenced by temperature, humidity, and wind direction. In Thailand the meteorological conditions vary for every season. Due to high solubility of formaldehyde and acetaldehyde, the washout ratios of these compounds together with episodic nature of precipitation events, indicate that wet deposition is expected to influence the concentration level of formaldehyde

and acetaldehyde in Bangkok. The concentration is high during the cold season due to lower temperatures and more stable conditions that

3) Photochemical reactions of formaldehyde and acetaldehyde occurs in the atmosphere through various mechanisms, such as reaction with hydroxyl radicals, ozone, hydroperoxyl radicals, and nitrate radicals. On the basis of the rate of constant for each of the reactions and the concentration of the reactants, the reaction with hydroxyl radical is considered to be the most important.

5.1.2 Task 2: To determine the concentration of carbonyl compounds In relation to traffic density.

1) The concentration of carbonyl compounds in Bangkok increased significantly due to rapid increase in gasohol consumption.

2) Good correlation between concentration of formaldehyde and acetaldehyde in ambient air and car density was obtained which indicate that vehicles fuelled with gasohol contribute to the emission of these compounds.

3) The concentration of formaldehyde and acetaldehyde were higher during the day time due to incomplete combustion from the vehicles using gasohol, as well as photochemical reactions of other Volatile Organic Compounds (VOCs). During the night time the concentration becomes lower due to sources reduction such as absence of solar radiation that enhance photochemical reactions and

decrease traffic density, which agree with the same study done by Possanzini et al., 1996.

4) The concentration of carbonyl compounds in the Bangkok were higher than Mabthaphut Industrial area, ERTC, Pathumthani (Rural area), and Suwarrnaphum International airport. This is due to very high traffic density in Bangkok compared with other areas in the country.

5.2 Recommendations for the improvement of air quality in Bangkok

The government's policy to replace the conventional gasoline to gasohol will cause high concentration of carbonyl compounds especially formaldehyde and acetaldehyde. In order to improve the air quality in Bangkok, some strategy and mitigation measures should be emphasized such as:

1) New Ambient Air Quality Standards for Toxic Substances such as formaldehyde, and acetaldehyde should be established in order to reduce toxic air pollutants from the use of gasohol in Thailand.

2) New and old cars should be equipped with catalytic converters that can trap both carbonyl compounds and primary pollutants. And the lifetime of the catalytic converters presently used should be evaluated due to switching of fuels.

3) Incentives should be provided to manufacturers of motorcycles to produce motorcycles equipped with catalytic converters to trap carbonyl compounds and other primary pollutants.

4) Stringent car and motorcycle inspection and maintenance should be strictly enforced based on hydrocarbons, aldehydes, and NOx certification.

5) Future studies also needs to consider photochemical impacts of increased levels of NOx and carbonyl compounds, because these pollutants will likely to increase ozone and oxidant levels which could effect the health of the people and damage vegetation.

6) Actual exposure to chemicals associated with fuels most commonly occur as exposure to complex chemical mixtures, rather than isolated chemicals, thus, it is important that the health effects of interaction between individual components of these mixtures be characterized in addition to health effects of the individual compounds.

7) There are presently large gaps in our knowledge of the health effects of exposures to complex mixtures of compounds associated with alternative fuels and gasoline, as well as the health effects associated with some individual compounds. It is therefore a need to conduct research and further develop and evaluate existing epidemiological data on human health effects from complex mixtures associated with fuel components.

8) The emission and atmospheric chemistry have already been the subjects of extensive study, and sophisticated models are available, significant uncertainties still remain. It is important to continue monitor the actual concentration levels of these atmospheric pollutants in order to observe the outcome of changes in vehicle type, usage of the different types of fuel composition, and to confirm the accuracy of model predictions.

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APPENDICES

Appendix A: Concentration of Carbonyl Compounds in 10 Sites in Bangkok during July 2007 to April 2008.

Appendix B: Calibration of the 15 carbonyl compounds studied.

Appendix C: Traffic Density in Chokchai 4 and DonMuang during May and June 2008.

Appendix D: Picture of the 10 sampling sites in Bangkok.

Appendix A: Concentration of Carbonyl Compounds in 10 Sites in Bangkok during July 2007 to April 2008.

ALDEHYDE (ug/m^3)	Bannongbon (RO1)										
	14/7/2007	9/8/2007	11/9/2007	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	5/4/2008	Average
Formaldehyde	4.04	7.2	4.26	5.8	16.6	10.7	11.5	11	10.1	10.5	9.17
Acetaldehyde	0.82	0.57	1.40	2.19	3.24	9.50	6.04	4.73	3.68	6.5	3.87
Acetone	2.41	7.1	1.18	6.02	5.71		8.69	8.89	7.27	6.39	5.96
Propionaldehyde	0.17		0.21	1.27		4.762	0.831	4.097	2.603	2.569	2.06
Crotonaldehyde	0.22	0.15	0.16	0.256	0.45	5.54	2.24	0.42	2.62	0.49	1.25
Butyraldehyde	0.77		0.17	0.311		0.752	1.592	4.838	4.095	0.984	1.69
Benzaldehyde	5.11		0.44		0.388	10.548	3.544	7.535	5.621	0.764	4.24
Isovaleraldehyde		0.886	0.47	0.173	0.388			0.521		0.833	0.55
Valeraldehyde			1.44	0.208		1.12	1.76	1.63		1.18	1.22
Hexanaldehyde	0.4	0.89	1.72	0.145	1.26	3.2	1.43	0.83	0.57	4.93	1.54

ALDEHYDE (ug/m^3)	Dindaeng (RO2)										
	14/7/2007	9/8/2007	11/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	5/4/2008	Average
Formaldehyde	7.96	7.25	5.84	7.60	19.20	23.30	30.90	14.90	11.50	14.50	14.30
Acetaldehyde	3.89	2.48	1.48	2.13	6.07	5.95	10.04	7.00	1.60	1.30	4.19
Acetone		6.09	1.10	5.18	8.44	7.59	8.80	6.89	0.85	0.36	5.03
Propionaldehyde	0.82	0.69	0.23	0.78	1.45	3.91	2.26	1.30	0.85	0.32	1.26
Crotonaldehyde	0.71		0.48		1.01	0.35					0.64
Butyraldehyde	0.6	0.57	0.13	0.14		1.18	5.59	2.92	0.70	0.30	1.35
Benzaldehyde		4.07	0.24	1.56	0.73	3.86	2.67	2.38	1.65	0.10	1.92
Isovaleraldehyde		0.57			0.73	4.46	0.48		0.12	0.48	1.14
Valeraldehyde	0.36	0.65	0.93	0.46		1.14	2.49	2.52	0.49	0.11	1.02
Hexanaldehyde	0.46	0.76	0.70		2.08	1.09	2.74	2.58	0.40	0.57	1.26

ALDEHYDE (ug/m^3)	DonMuang (RO3)									
	14/7/2007	9/8/2007	11/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	5/4/2008	Average
Formaldehyde	4.57	7.45	4.26	4.82	11.71	12.00	6.78	12.15	13.77	11.51	8.90
Acetaldehyde	0.81	0.53	1.51	2.50	3.64	0.93	6.13	1.94	1.65	1.08	2.07
Acetone	4.21	9.59	1.12		4.87	0.49	4.24	1.78	1.27		3.45
Propionaldehyde	0.32	0.76	0.24	3.04		0.27	0.71	0.78	0.73	0.21	0.78
Crotonaldehyde		0.14	0.51		0.71				0.62		0.50
Butyraldehyde	1.03	0.72	0.13	0.40		0.13	1.83	0.84	0.16	0.24	0.61
Benzaldehyde	0.14	3.89	0.21		0.47	0.24	1.50	1.52			1.14
Isovaleraldehyde	0.40		0.19	0.40	0.47	0.10	1.68		0.75	0.24	0.53
Valeraldehyde		0.87	1.04	0.20		0.10	0.73	0.23	0.23		0.49
Hexanaldehyde	0.32	0.84	0.86	0.24	1.47	0.34	2.33	0.91	0.15	0.43	0.79

ALDEHYDE (ug/m^3)	Transportation (RO4)										
	14/7/2007	9/8/2007	29/9/1950	7/10/1900	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	1.73	3.53	9.26	5.20	18.58	15.99	16.3	14.67	11.77	15.28	11.24
Acetaldehyde	0.14	1.15	3.96	13.62	10.04	10.59	8.21	11.33	5.99	1.15	6.62
Acetone	5.48	16.5	1.26	1.80	15.13	12.15	10.6	10.90	4.50	0.62	7.90
Propionaldehyde	0.11	0.51	0.57		13.23	5.01	1.63	7.51	4.19	0.29	3.67
Crotonaldehyde			1.25		0.72	0.98	5.04	4.36	0.21	0.10	1.81
Butyraldehyde		1.13	0.23	0.30	1.87	0.54	3.17	0.77	1.80	0.82	1.18
Benzaldehyde			0.68	1.62	1.52	6.70	1.00	7.99	11.66	0.11	3.91
Isovaleraldehyde	1.56	4.39	0.33			1.90	1.80	0.76			1.79
Valeraldehyde		1.14	1.77					4.88	1.14	0.33	1.85
Hexanaldehyde	0.29	0.65	1.16	3.74	3.23	4.35	0.24	9.55	2.98	0.44	2.66

ALDEHYDE (ug/m^3)	Chokchai 4 (RO5)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	7.41	10.60	5.26	7.10	19.9	20.9	19.12	13.8	18.9	14.9	13.8
Acetaldehyde	2.43	3.30	2.93	3.40	13.6	14.2	9.34	9.25	4.81	1.10	6.43
Acetone			2.17	13.5		18.5	11.16	10.94	28.69	0.50	12.2
Propionaldehyde		0.76	0.44	3.99	8.57	15.2	0.26	3.74	0.52	0.30	3.75
Crotonaldehyde	0.22	0.31	0.44	0.15	0.42	0.73	1.83	0.35	0.62		0.56
Butyraldehyde	0.39		0.16	0.50	0.60	8.71	0.53	4.61	1.25	0.13	1.88
Benzaldehyde	4.15	9.16	0.72		7.36	1.48	3.29	7.51	1.11	0.11	3.88
Isovaleraldehyde	0.47	0.50			2.26	4.18	0.57	0.52	0.87	0.29	1.21
Valeraldehyde	0.25	0.72	3.09		3.03	5.91	1.92	2.87	1.25		2.38
Hexanaldehyde	0.46	1.16	2.88	1.04	9.48	8.64	0.26	3.98	2.73	0.65	3.13

ALDEHYDE (ug/m^3)	Bangkapi Sukum School (RS1)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	3.88	3.99	4.10	6.74	26.6	10.2	10.3	8.43	12.0	12.1	9.84
Acetaldehyde	1.02	1.53	2.57	3.96	11.0	3.78	5.73	4.90	7.76	5.88	4.81
Acetone	4.48	7.42	2.17	7.77		6.4	5.95	5.19	5.99	6.04	5.71
Propionaldehyde	0.30	0.54	0.33	4.79	8.956	2.81	0.73	0.69	3.81	4.10	2.71
Crotonaldehyde	0.36		0.39	0.39	0.42	0.28	2.49		3.25	3.37	1.37
Butyraldehyde	0.31	1.1	0.25	0.66		2.88	0.25	0.81	0.63	1.09	0.89
Benzaldehyde	7.14	15.4	0.42			1.42	2.66	0.26	6.89	0.59	4.35
Isovaleraldehyde			0.64		2.34	0.55	0.51		0.80	6.04	1.81
Valeraldehyde		0.80	3.31			0.10	1.33	1.25	1.94	1.70	1.49
Hexanaldehyde		0.71	2.84	5.99	3.101	1.44	1.23	0.51	2.35	2.92	2.34

ALDEHYDE (ug/m^3)	Bodin School (RS2)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	3.89	3.85	3.39	4.28	22.5	16.3	16.4	8.86	11.5	11.7	10.3
Acetaldehyde	1.26	1.79	2.32	3.58	12.9	9.17	8.21	5.79	1.81	3.29	5.01
Acetone	7.77	4.1	1.80	7.71		15.5	10.6	10.3	1.45	10.5	7.76
Propionaldehyde	0.47	0.68	0.35	1.66	7.55	5.81	1.63	3.50		1.32	2.55
Crotonaldehyde		0.11	0.22	0.40	0.89	1.25		5.47	0.979	2.51	1.48
Butyraldehyde	0.16	1.20	0.10	2.70		2.03	5.04	0.32		1.88	1.68
Benzaldehyde	4.84	13.2	0.71	3.36	1.83	4.83	3.17	4.01	1.18	1.38	3.85
Isovaleraldehyde	0.46	0.60		2.78		4.75	1.00	1.25		2.48	1.90
Valeraldehyde	0.37	0.64	3.09	0.71		2.39	1.80	2.08	0.154	0.78	1.33
Hexanaldehyde	0.58	0.62	2.70	7.81	5.54	2.82	0.24	6.09	0.352	3.28	3.00

ALDEHYDE (ug/m^3)	Wat Singh (RS3)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	4.08	3.74	4.40	8.22	18.6	7.31	17.0	9.31	12.6	11.88	9.72
Acetaldehyde	2.37	1.04	2.40	3.09	11.0	6.39	9.99	4.68	0.67	6.23	4.79
Acetone		15.5	2.12	4.61	17.6	13.41	10.6	10.07		6.60	10.1
Propionaldehyde	0.37	0.43	0.35	4.44	6.58	1.00	2.03	1.28	0.27	4.06	2.08
Crotonaldehyde	0.18	0.21	0.62	0.12	0.30	1.00		0.59	0.028	5.69	0.97
Butyraldehyde	0.57	2.3	0.23	0.46	1.72		0.48	4.23	0.201	1.19	1.27
Benzaldehyde	4.91		0.46			11.4	3.61	3.70		0.45	4.09
Isovaleraldehyde	2.71	0.22	0.42		1.44		0.83		0.367	8.61	2.09
Valeraldehyde	0.17		1.41				1.94	0.62	0.305	1.91	1.06
Hexanaldehyde	0.61	0.78	0.84	5.52	3.65	3.50	2.78	4.22	0.502	2.78	2.52

ALDEHYDE (ug/m^3)	Bangkok Naval Base (RS4)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	2.82	5.19	2.99	9.18	8.37	10.6	11.5	6.82	12.6	11.5	10.6
Acetaldehyde	0.86	1.51	2.16	5.07	5.58	5.91	10.2	5.89	1.16	5.32	5.7
Acetone	4.98	10.19	1.56	8.76		8.56	7.32	7.16	0.45	6.91	6.1
Propionaldehyde	0.44	0.60	0.14	6.37	0.32	4.29	1.37	3.08	0.208	4.06	2.6
Crotonaldehyde	0.17	0.17	0.24	0.12		0.75	1.02	0.62		1.46	1.0
Butyraldehyde	0.52	0.54	0.57	0.78	1.18	5.78	1.63	3.16	0.20	0.84	2.3
Benzaldehyde		3.25	0.24	2.38	0.66	6.36	2.99	1.70		0.38	2.9
Isovaleraldehyde	0.42	0.64			1.15	1.28	0.37	4.60	0.26	5.80	2.5
Valeraldehyde	0.46	0.76	1.47		2.99	1.63	1.67	0.73		1.56	1.4
Hexanaldehyde	0.55	0.76	2.60	5.11	3.52	0.15	2.18	0.61	2.50	1.8	1.4

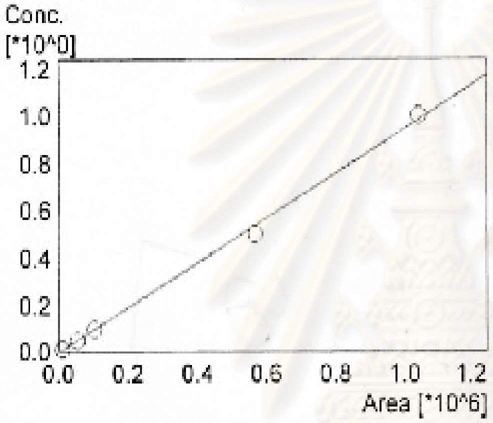
ALDEHYDE (ug/m^3)	Prachanukul School (RS5)										
	14/7/2007	9/8/2007	29/9/1950	18/10/2007	27/11/2007	21/12/2008	7/1/2008	16/2/2008	29/3/2008	6/4/2008	Average
Formaldehyde	3.00	3.71	2.35	7.61	11.8	12.8	11.9	10.4	16.5	11.4	9.16
Acetaldehyde	0.82	0.99	1.86	2.59	10.1	9.79	6.10	7.73	5.55	1.13	4.67
Acetone	4.76	8.17	0.72	10.66	14.5		6.88	10.21		1.38	7.16
Propionaldehyde	0.22	0.40	0.22	2.38	3.10	7.47	1.18	3.08	1.28	0.81	2.01
Crotonaldehyde	0.12	0.13	1.12	0.94		0.60		0.21	0.62	0.73	0.56
Butyraldehyde	1.22	1.03		0.38	0.49	6.37		3.37	0.70	0.21	1.72
Benzaldehyde	4.47		0.28			6.87	2.33	5.81	1.04		3.47
Isovaleraldehyde		0.29				1.61	0.25	1.18	0.69	1.16	0.86
Valeraldehyde		0.69	0.55	2.87		0.24	1.44	3.18	3.36		1.76
Hexanaldehyde	0.30	0.86	0.68	0.79	5.26	1.65	1.72	4.71	1.35	2.07	1.94

Appendix B: Calibration of the 15 carbonyl compounds studied.

==== Shimadzu LCsolution Calibration Curve ====

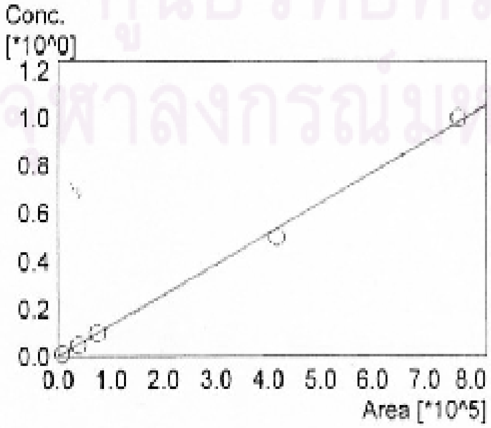
<Calibration Curve>

ID# : 1
Name : Formaldehyde
Quantitative Method : External Standard
Function : f(x)=9.43605e-007*x+0
Rr1=0.9989998 Rr2=0.9980006
MeanRF:9.31349e-007 RFSD:3.92065e-008 RFRSD:4.20964
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



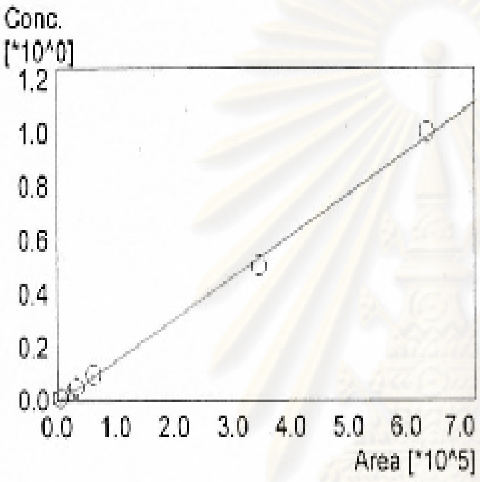
#	Conc (Ratio)	Area	Area
1	0.010	11096.1	11096
3	0.050	53550.6	53551
4	0.100	102346.6	102347
5	0.500	565765.9	565766
6	1.000	1040578.9	1040579

ID# : 2
Name : Acetaldehyde
Quantitative Method : External Standard
Function : f(x)=1.28214e-006*x+0
Rr1=0.9989248 Rr2=0.9978507
MeanRF:1.28547e-006 RFSD:5.23259e-008 RFRSD:4.07057
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



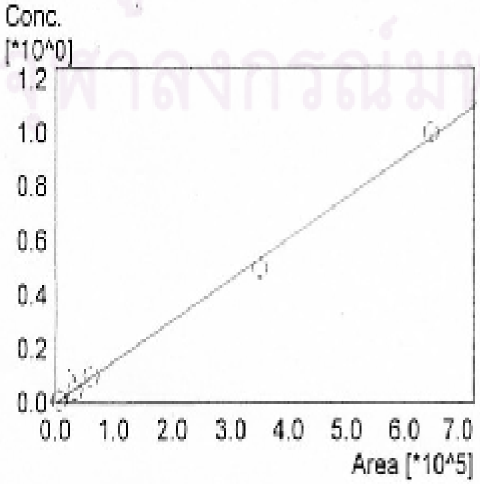
#	Conc (Ratio)	Area	Area
1	0.010	7766.7	7767
3	0.050	38583.9	38584
4	0.100	74686.7	74687
5	0.500	417150.0	417150
6	1.000	765477.9	765478

ID# : 3
Name : Acetone
Quantitative Method : External Standard
Function : f(x)=1.54333e-006*x+0
Rr1=0.9990403 Rr2=0.9980815
MeanRF:1.5291e-006 RFSD:5.92127e-008 RFRSD:3.87239
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



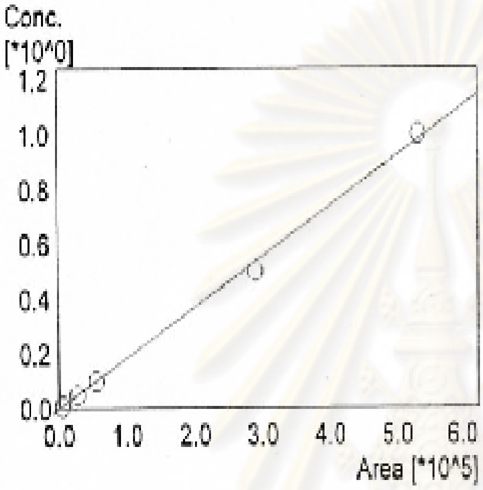
#	Conc (Ratio)	Area	Area
1	0.010	6655.8	6656
3	0.050	32770.4	32770
4	0.100	62547.2	62547
5	0.500	345455.9	345456
6	1.000	636490.4	636490

ID# : 4
Name : Acrolein
Quantitative Method : External Standard
Function : f(x)=1.52067e-006*x+0
Rr1=0.9988975 Rr2=0.9977963
MeanRF:1.52041e-006 RFSD:8.3231e-008 RFRSD:5.47426
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



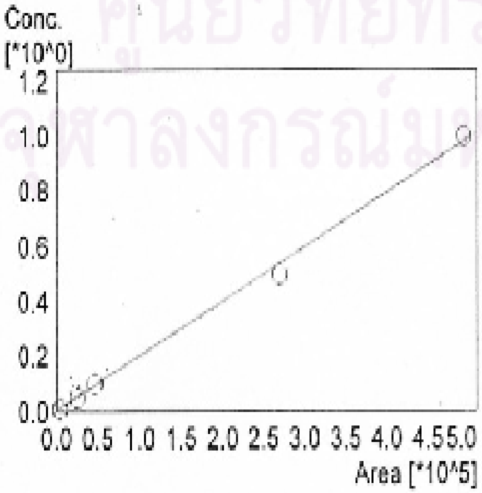
#	Conc (Ratio)	Area	Area
1	0.010	6784.8	6785
3	0.050	33007.8	33008
4	0.100	60875.9	60876
5	0.500	351693.6	351694
6	1.000	645586.4	645586

ID# : 5
Name : Propionaldehyde
Quantitative Method : External Standard
Function : f(x)=1.84703e-006*x+0
Rr1=0.9989558 Rr2=0.9979127
MeanRF:1.79428e-006 RFSD:6.23682e-008 RFRSD:3.47595
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



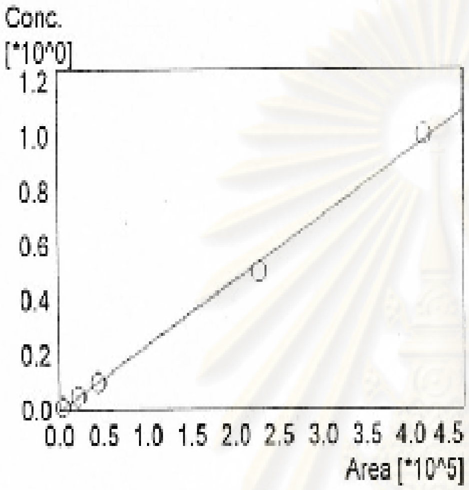
#	Conc (Ratio)	Area	Area
1	0.010	5729.4	5729
3	0.050	27567.8	27568
4	0.100	55467.3	55467
5	0.500	289744.7	289745
6	1.000	530850.2	530850

ID# : 6
Name : Crotonaldehyde
Quantitative Method : External Standard
Function : f(x)=1.9848e-006*x+0
Rr1=0.9988699 Rr2=0.9977411
MeanRF:2.05816e-006 RFSD:1.6826e-007 RFRSD:8.17526
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



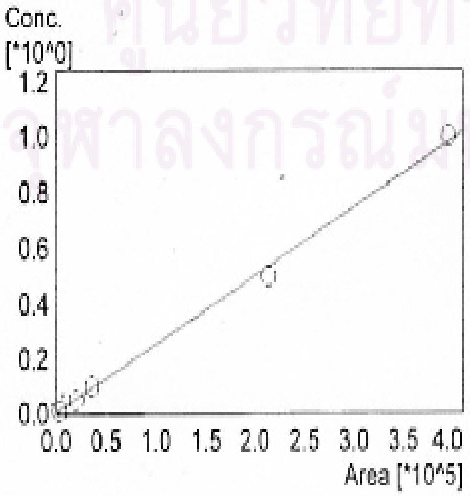
#	Conc (Ratio)	Area	Area
1	0.010	4359.8	4360
3	0.050	25335.2	25335
4	0.100	46578.5	46579
5	0.500	269598.6	269599
6	1.000	494544.6	494545

ID# : 7
Name : Butyraldehyde
Quantitative Method : External Standard
Function : f(x)=2.35874e-006*x+0
Rr1=0.9988751 Rr2=0.9977515
MeanRF:2.33543e-006 RFSD:1.10437e-007 RFRSD:4.72877
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



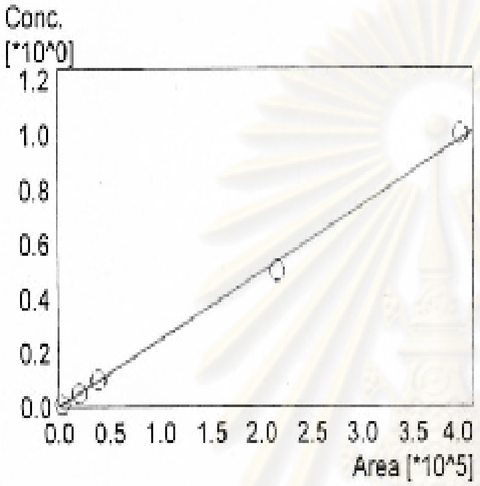
#	Conc (Ratio)	Area	Area
1	0.010	4039.3	4039
3	0.050	21440.5	21441
4	0.100	44197.3	44197
5	0.500	227360.4	227360
6	1.000	415331.0	415331

ID# : 8
Name : Benzaldehyde
Quantitative Method : External Standard
Function : f(x)=2.48528e-006*x+0
Rr1=0.9990656 Rr2=0.9981321
MeanRF:2.62408e-006 RFSD:2.63901e-007 RFRSD:10.0569
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



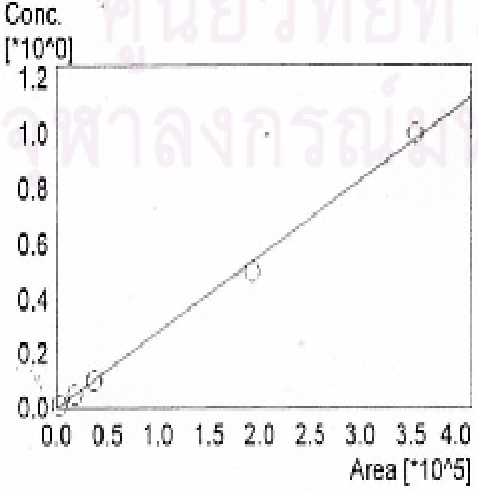
#	Conc (Ratio)	Area	Area
1	0.010	3327.4	3327
3	0.050	20165.6	20166
4	0.100	36091.1	36091
5	0.500	213728.0	213728
6	1.000	395980.8	395981

ID# : 9
Name : Isovaleraldehyde
Quantitative Method : External Standard
Function : f(x)=2.47095e-006*x+0
Rr1=0.9990678 Rr2=0.9981365
MeanRF:2.55582e-006 RFSD:2.04351e-007 RFRSD:7.99549
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



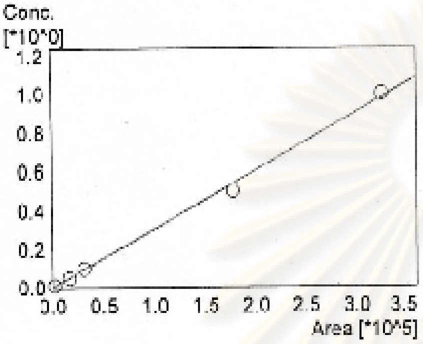
#	Conc (Ratio)	Area	Area
1	0.010	3475.5	3475
3	0.050	20162.7	20163
4	0.100	38651.7	38652
5	0.500	215425.4	215425
6	1.000	397808.3	397808

ID# : 10
Name : Valeraldehyde
Quantitative Method : External Standard
Function : f(x)=2.76766e-006*x+0
Rr1=0.9990519 Rr2=0.9981046
MeanRF:2.87662e-006 RFSD:3.55943e-007 RFRSD:12.3737
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



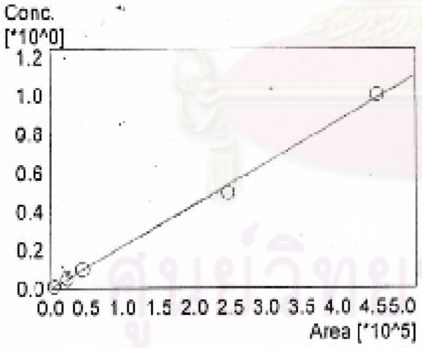
#	Conc (Ratio)	Area	Area
1	0.010	2860.3	2860
3	0.050	18099.9	18100
4	0.100	36906.0	36906
5	0.500	192596.6	192597
6	1.000	354758.7	354759

```
ID#                      : 11
Name                     : o-Tolualdehyde
Quantitative Method      : External Standard
Function                 : f(x)=3.01149e-006*x+0
                           Rr1=0.9989045   Rr2=0.9978103
                           MeanRF:3.22516e-006  RFSD:4.8142e-007   RFRSD:14.927
FitType                  : Linear
ZeroThrough              : Through
WeightedRegression       : None
Detector Name            : Detector A
```



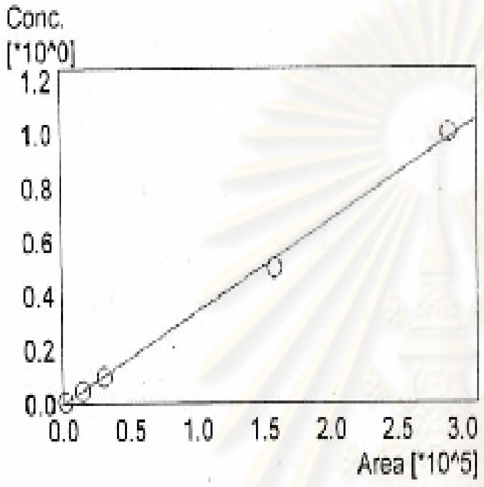
#	Conc (Ratio)	Area	Area
1	0.010	2466.4	2466
3	0.050	16582.7	16583
4	0.100	31520.2	31520
5	0.500	177590.0	177590
6	1.000	325933.7	325934

```
ID#                      : 12
Name                     : m,p-Tolualdehyde
Quantitative Method      : External Standard
Function                 : f(x)=2.15528e-006*x+0
                           Rr1=0.9990894   Rr2=0.9981797
                           MeanRF:2.13048e-006  RFSD:8.55509e-008   RFRSD:4.01558
FitType                  : Linear
ZeroThrough              : Through
WeightedRegression       : None
Detector Name            : Detector A
```



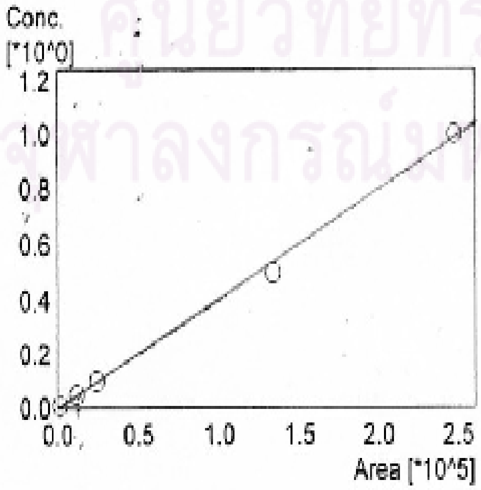
#	Conc (Ratio)	Area	Area
1	0.010	4845.5	4845
3	0.050	23328.9	23329
4	0.100	44884.6	44885
5	0.500	246987.3	246987
6	1.000	455993.2	455993

ID# : 13
Name : Hexanaldehyde
Quantitative Method : External Standard
Function : f(x)=3.38931e-006*x+0
Rr1=0.9989252 Rr2=0.9978516
MeanRF:3.68607e-006 RFSD:8.44698e-007 RFRSD:22.9159
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



#	Conc (Ratio)	Area	Area
1	0.010	1928.7	1929
3	0.050	14893.9	14894
4	0.100	30639.5	30640
5	0.500	157824.3	157824
6	1.000	289304.5	289305

ID# : 14
Name : 2,5-Dimethylbenzaldehyde
Quantitative Method : External Standard
Function : f(x)=3.97837e-006*x+0
Rr1=0.9990413 Rr2=0.9980836
MeanRF:4.46198e-006 RFSD:9.48629e-007 RFRSD:21.2603
FitType : Linear
ZeroThrough : Through
WeightedRegression : None
Detector Name : Detector A



#	Conc (Ratio)	Area	Area
1	0.010	1633.0	1633
3	0.050	11772.8	11773
4	0.100	24064.5	24065
5	0.500	133802.3	133802
6	1.000	247108.9	247109

Appendix C: Traffic Density in Chokchai 4 and DonMuang during May and June 2008.

Traffic Density in Chokchai 4 May 2008 00:05 - 23:55 (24 hrs.)

Date	Cars	Taxi	Pick-up	Motorcycle	Van	Passenger Bus	TOTAL
13-May-08	28,080	18,825	17,401	10,338	3,833	4,079	82,556
14-May-08	29,393	20,887	21,387	10,703	3,805	4,030	90,205
15-May-08	24,694	19,484	17,322	9,864	3,645	4,023	79,032
16-May-08	28,224	18,734	17,329	10,102	3,858	4,161	82,408
17-May-08	27,937	18,916	17,473	10,675	3,809	3,998	82,808
18-May-08	27,958	17,903	17,093	11,433	3,749	3,931	82,067
19-May-08	27,947	18,409	17,283	11,054	3,779	3,964	82,436
AVERAGE	27,748	19,023	17,898	10,596	3,783	4,027	83,073

AVERAGE Daily Traffic Density 83,073

Traffic Density in Chokchai 4 June 2008 00:05 - 23:55 (24 hrs.)

Date	Cars	Taxi	Pick-up	Motorcycle	Van	Passenger Bus	TOTAL
6-Jun-08	28,028	20,844	18,094	10,644	3,542	4,267	85,419
7-Jun-08	27,708	19,801	17,623	9,720	3,433	4,123	82,408
8-Jun-08	27,993	18,911	17,557	9,915	3,504	4,050	81,930
9-Jun-08	28,116	18,973	17,268	10,791	3,779	4,178	83,105
10-Jun-08	27,777	18,914	17,145	10,576	3,938	4,106	82,456
11-Jun-08	27,985	18,977	17,330	11,021	3,837	4,036	83,186
12-Jun-08	27,931	19,745	17,237	10,798	3,887	4,071	83,669
AVERAGE	27,934	19,452	17,465	10,495	3,703	4,119	83,168

AVERAGE Daily Traffic Density 83,168

Car Density DonMuang May 19-25 2008 (7Days)						
Day	Date	Motorcycle	Car	Pick-up/Van	Taxi	Remark
Monday	19-May-08	27826	3175	3200	963	00:01-23:59 hrs
Tuesday	20-May-08	24782	2866	3607	1052	00:09-23:55 hrs
Wednesday	21-May-08	20701	3331	3729	1018	00:10-23:55 hrs
Thursday	22-May-08	24311	2760	3594	1167	00:10-23:55 hrs
Friday	23-May-08	23239	3080	4082	1247	00:10-23:55 hrs
Saturday	24-May-08	24645	3546	3384	1372	00:10-23:55 hrs
Sunday	25-May-08	23576	3716	3477	1332	00:10-23:54 hrs
Average		24,154	3,211	3,582	1,164	
Total vehicles per day 32,111						

Car Density DonMuang June 9-15 2008 (7Days)						
Day	Date	Motorcycle	Car	Pick-up/Van	Taxi	Remark
Monday	9-Jun-08	27826	3175	3200	963	00:09-23:54 hrs
Tuesday	10-Jun-08	24065	3347	3405	1110	00:09-23:55 hrs
Wednesday	11-Jun-08	26448	2944	3262	1033	00:10-23:55 hrs
Thursday	12-Jun-08	26448	2944	3262	1033	00:10-23:55 hrs
Friday	13-Jun-08	27133	2891	3332	1089	00:10-23:55 hrs
Saturday	14-Jun-08	26748	2640	3598	990	00:10-23:55 hrs
Sunday	15-Jun-08	23974	3502	3504	1318	00:10-23:55 hrs
Average		25,190	3,112	3,375	1,104	
Total vehicles per day 33,121						

Appendix D: Photo of the 10 sampling sites in Bangkok.

Sampling Site: Bannongbon School   (RO1)

Sampling Site: Dindaeng   (RO2)

Sampling Site: DonMuang District Office   (RO3)

Samppling Site: Department of Transportation (RO4)

Sampling Site: Chokchai 4 (RO5)

Sampling Site: Bangkapi Sukum School (RS1)

Sampling Site: Bodin Decha School   (RS2)

Sampling Site: Wat Singh   (RS3)

Sampling Site: Bangkok Naval Base (RS4)

Sampling Site: Prachanukul School

BIOGRAPHY

NAME	Mrs. Daisy Morknoy
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