STUDY OF MERCUY DEPOSITION PROCESSES IN THAILAND INTEGRATING EMISSION SOURCE CHARACTERIZATION AND ATMOSPHERIC MODELING

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A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN ENVIRONMENTAL TECHNOLOGY

THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
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ABSTRACT

Mercury (Hg) is considered to be a Hazardous Air Pollutant (HAP), and its deposition results in adverse effects to both human health and the ecosystem. Recent global assessment of atmospheric Hg fate indicated a relatively high level of Hg deposition flux, which is directly linked to health risk in the Northern of Thailand. This observation raised questions about the emission-to-deposition processes. In this regard, it is necessary to investigate several involved factors, such as source characteristics, meteorological conditions, and chemical transformation driving deposition processes.

Thailand has various Hg anthropogenic atmospheric emissions sources, such as coal-fired power plants, cements, large scale gold mining. In this study, characteristics of anthropogenic atmospheric Hg emissions for the year 2010 were presented. The calculations were based mostly on the bottom up approach. The activity data were obtained from official sources including governmental reports and databases. The emission factors of Hg species were assessed from local sources or adapted from literature review with proper adjustments to well reflect emissions behaviors of various sources in Thailand. It was found that in year 2010, total atmospheric Hg emissions were 20,495.2 kg, which 79.0% from natural sources, 19.7% from anthropogenic sources, and 1.2% from biomass open burning. Within Hg speciation, Hg^0, Hg^{2+} and Hg^P accounted for 91.7 %, 6.5%, and 7.8 % respectively.

To better understand the mechanism of Hg deposition in the case of Thailand, a coupled model consisting of a meteorological model (i.e., MM5) and an air quality model (i.e., CAMx) was used. To access seasonal variation, 4 one-month simulations (here are March, May, August, and November 2010) were performed. In general, all options captured the temporal variation of meteorological parameters in Thailand which are generally influenced by monsoon. The comparison with 3 hourly data with Thai Meteorological Department indicated that reasonable agreement was found. Among several sets of investigated physical options, the combination of Grell, MRF, Simple ice, Cloud radiation scheme, and Five layer soil model had better agreement with observation, compared to other options.

Emissions of Hg as well as other species, such as NO_X, CO, SO_2, NMVOC, NH_3, PM_{10}, $PM_{2.5}$, OC, and BC, from both anthropogenic natural sources, and biomass in interested domains (inside and outside Thailand) were accessed in the year 2010 and then processed to input into the CAMx. Emissions were high in March due to biomass burning activity, and generally high in May due to the peak in power generation in the country during the summer period. Simulations of different months (March, May, August, and November 2010) showed that relatively high Hg concentration, mostly located in the northern of Thailand, is found in March and November, 2010. Of note, output of this work was not directly performed by in pair comparing with observations because firstly, there was no record of Hg concentration or deposition in study domain. Monthly average total Hg concentrations ranged between 1.7-2.6 ng/m^3 which is not far from yearly average of 1.7-2.0 ng/m^3 as output from global model and from samplings of 2.04 – 2.43 ng/m^3 in the northern of Thailand during March and April, 2010. Monthly accumulated Hg deposition in the northern of Thailand was up to 2.4 g/km^2/month, which was approximately 30 g/km^2/year in range with 20-50g/km^2/year found in HTAP (2010).

Sensitivity test of Hg deposition on emissions by disable Hg emissions inside domain 2 indicated that most of Hg concentration and deposition inside Thailand domain caused in mass inflow. Inflow and out flow of Hg species were analyzed. Transport budget of Hg^0 is relatively small and positive for all simulation months, indicating net transport of Hg speciated emissions out of the domain while that of Hg^{2+} and Hg^P is relatively high and negative, indicating net removal within the domain.

Keywords: Mercury, emissions, deposition, modeling, Thailand

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CONTENTS

CONTENTS (CONT')

CONTENTS (CONT')

CONTENTS (CONT')

LIST OF TABLES

LIST OF TABLES (CONT')

LIST OF FIGURES

CHAPTER 1
INTRODUCTION

This chapter presents general information as well as the rationale or the motivation of this research. It also provides the objectives and the scope of the work, and the main expected outputs/outcome.

1.1. Introduction

1.1.1. Studied Domain

The following sections provide general information on Thailand e.g., geo-socio-economic characteristics, climate and weather, as well as air quality management and potential sources of atmospheric emissions. Thailand is located in the tropical Southeast area between latitudes 5° 37'N to 20° 27'N and longitudes 97° 22'E to 105° 37'E. It is bordered to the north by Burma and Laos, to the east by Laos and Cambodia, to the south by the Gulf of Thailand and Malaysia, and to the west by the Andaman Sea and the southern of Burma. Thailand's maritime boundaries include Vietnam in the Gulf of Thailand to the southeast and Indonesia and India in the Andaman Sea to the southwest (Figure 1.1). Thailand has 5 regions with total 513,000 km^2 with capital city is Bangkok. The central part consists of low level plain and Chao Phraya River while the eastern part is adjacent to the Gulf of Thailand. The northern part consists of hill and mountain while in the northeastern part consists of high level plain called northeastern plateau. Most of the industrial activities located in the central and eastern while the northern and northeastern regions concern about biomass and forest fires.

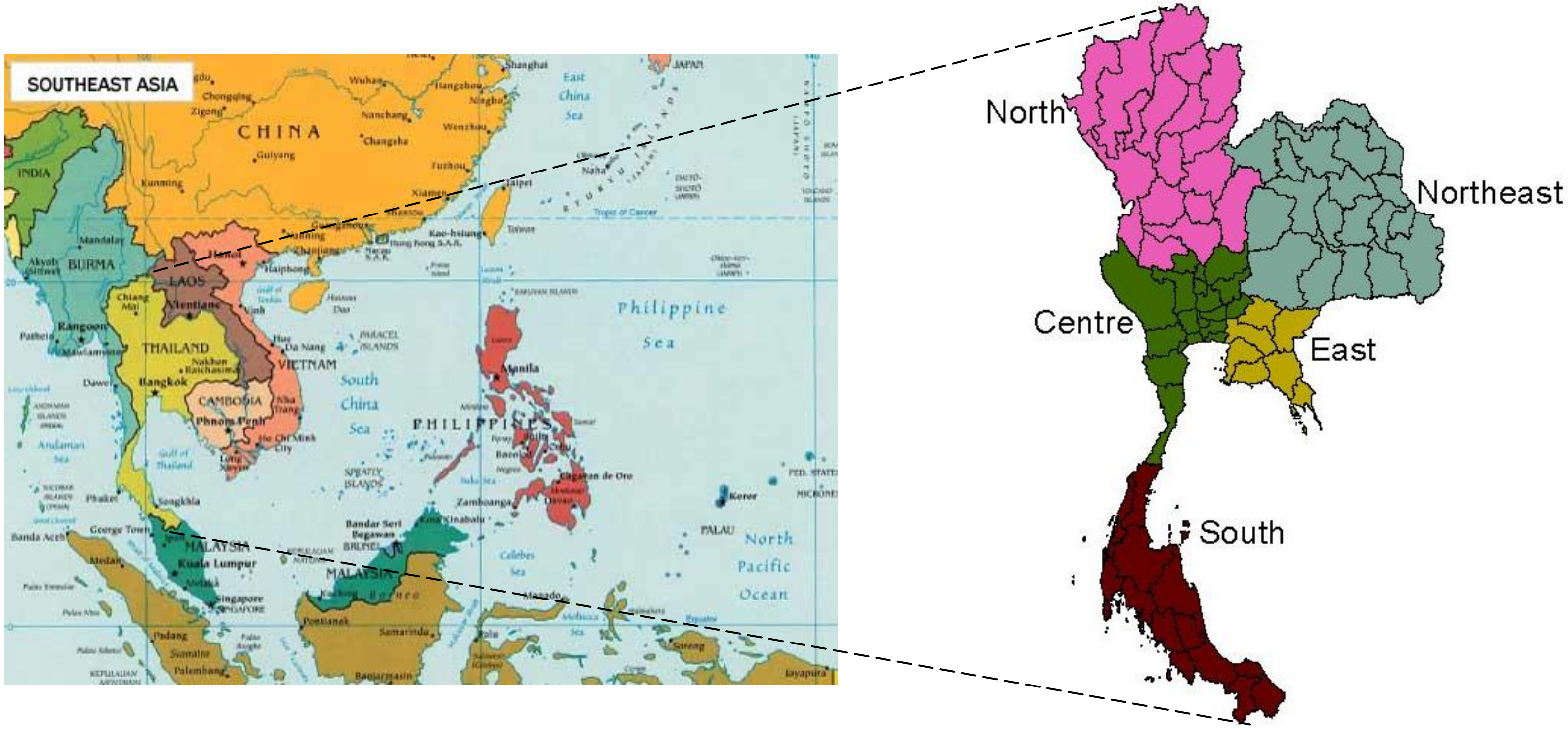


Figure 1.1: Map of Thailand in Southeast Asia Region (Left), and Thailand and its Political Boundaries (Right)

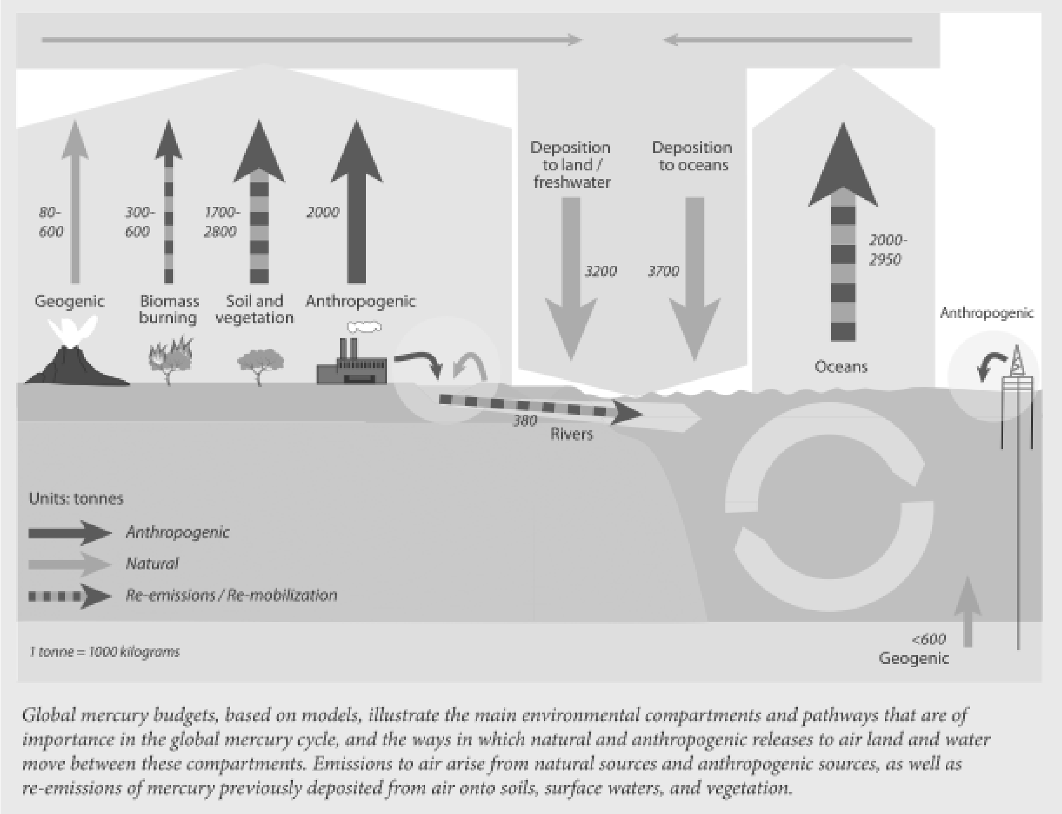
1.1.2. Mercury in General

1.1.2.1. Characteristics of Mercury

Mercury (abbreviation symbol “Hg”) is a heavy silvery metal with an atomic number of 80 and an atomic molecular weight of 200.6 gram/mol. It has a unique characteristic in that it can be in liquid form at room temperature and pressure. Physical properties of Hg are as follows: boiling point 357 ^{o}C, freezing point -38.7 ^{o}C, melting point -39^{o}C, density 13.6 g/mol. After the industrial revolution since 1960s, Hg is well-known and widely-used in many industries as metal (e.g., in extraction of gold and silver, in thermometer, in fluorescent lamps, in dental amalgam fillings) or as catalyst (e.g., in batteries, caustic soda) (UNEP, 2002). Hg exists in forms of organic and inorganic Hg. Hg is original emitted in inorganic form, existing in the atmosphere as 3 species (i.e., Hg element (Hg^0), Hg reactive gaseous (Hg^{2+}), and Hg particulate (Hg^P)). Once emitted from the sources, depending on its speciation (Hg^0, Hg^{2+}, and Hg^P), it has different characteristic and atmospheric lifetime. Hg^0 is insoluble in water and quite inert therefore it has a longest atmospheric life time (from 0.5 – 2 years) among its speciation. Hg^0 is also subject to long range transport which could cause trans-pacific effects (Strode *et al.*, 2008). In contrast, Hg^{2+} is water soluble and reactive; therefore, it is subject to quick transform and remove/deposit near the emitted sources. Similarly, Hg^P can be interacted with other particle and deposited near the emitted sources. The concern of Hg is mostly after deposition, where inorganic Hg is converted to organic Hg (i.e., methyl Hg) under the present of bacteria. Such organic Hg is persistence and accumulated in ecosystem and cause adverse effects to living creature and higher level predators.

1.1.2.2. Mercury Cycle in the Ecosystem: Water –Soil – Air – Fish

Hg naturally occurs in the Earth’s crust. It is emitted and cycled in several pathways such as air, water, soil as shown in (Figure 1.2). It can be emitted unintentionally through extraction/combustion of earth crust element such as fossil fuels (e.g., coal), metals (e.g., copper, lead, and gold), or intentionally through mined (e.g., Hg mining and primary production) and uses of Hg as key material or catalyst during industrial processes (e.g., caustic soda, battery production). Atmospheric emissions are subject to transport and transform and deposit to other ecosystems such as soil, water, and vegetation. Hg in these ecosystems is converted to CH_3Hg which is highly toxic which are gradually absorbed by living creatures from low to high level predator (i.e., fish) in food chain. Once presented in ecosystems, Hg is persistent and bio-accumulated which results adverse effects. In next section, more details on Hg adverse effects to human health are presented.



Global mercury budgets, based on models, illustrate the main environmental compartments and pathways that are of importance in the global mercury cycle, and the ways in which natural and anthropogenic releases to air land and water move between these compartments. Emissions to air arise from natural sources and anthropogenic sources, as well as re-emissions of mercury previously deposited from air onto soils, surface waters, and vegetation.

Figure 1.2: Hg Cycle and Hg Global Budget (UNEP, 2013)

As seen in Figure 1.2, on a global scale, sources of Hg emissions include anthropogenic and natural as well as re-emissions/re-mobilization (dominant). Sinks of Hg emissions include deposition to land/freshwater and ocean.

1.1.2.3. Adverse Effects of Mercury to Human Health and Ecosystems

In the US Clean Air Act amendments of 1990, Hg was listed specifically as a hazardous air pollutant due to its adverse effects on humans and ecosystems (United State Environmental Pollution Agency, 1997; Selin, 2011). According to a report by the US EPA (United State Environmental Pollution Agency, 1997), though it depends on several factors (chemical form of Hg, dose, age and health of exposed person, duration and route of exposure), some adverse effects of Hg containing species can be listed in the following:

- CH_3Hg causes impaired neurological development of fetuses, infants, and children.
- Elemental (metallic) mercury primarily causes health effects when it is breathed as a vapor where it can be absorbed through the lungs, causing some symptoms, such as tremors, emotional changes (e.g., mood swings, irritability, nervousness, excessive shyness), insomnia, neuromuscular changes (such as weakness, muscle atrophy, twitching), headaches, disturbances in sensations, changes in nerve responses, and performance deficits on tests of cognitive function. At higher exposures there may be kidney effects, respiratory failure and death. High exposures to inorganic mercury may result in damage to the gastrointestinal tract, the nervous system, and the kidneys.

Several case studies about the effects of Hg have been done (Ui, 1992; Sullivan, 2005; Umbangtalad *et al.*, 2007; Hani, 2010).

1.2. Rationale / Problem Statement

Hg is a hazardous substance, as its deposition can be harmful to human health and ecosystems (US-EPA, 1997). There is much evidence of about the Hg content in contaminated human hair, fish, soil, and water (Suckcharoen and Lodenius, 1980; Zhang and Wong, 2007). One of the classic examples of Hg exposure to living creatures is Minamata disease in Japan during 1930-1970 which caused fishes as well as fish predators including human to be suffered severe Hg poisoning deformities and death (Ui, 1992). Since 1989, Hg as has been listed hazardous pollutant under Clean Air Act Amendments of 1990 due to potentially significant effects on human health. Understanding the fate of Hg emission is important to further investigate emission control policy and health impacts. In order to access or predict organic Hg accumulated in the ecosystems, the quantitatively amount of inorganic Hg transportation and deposition in the ecosystems is required.

To do so, the monitoring and the sampling of information are much required to obtain measurable values that can be used: (1) Data analysis: to show air concentration at the specific time and space; and (2) Modeling evaluation: to compare between simulation and observation of air concentration. However, monitoring and sampling information is often not available, especially in Asia in general and Thailand in particular, due to resource limitation.

Alternatively, air quality modeling has been widely used to simulate for investigation of Hg transformation pathways such as transport, transformation, and deposition of Hg concentration in the atmosphere (Ryaboshapko *et al.*, 2007; Ryaboshapko *et al.*, 2007). According to recent modeling studies of Hg deposition in the Northern Hemisphere (Travnikov, 2005; Pirrone and Keating, 2010) or the globe (Selin *et al.*, 2007; Holmes *et al.*, 2010; Corbitt *et al.*, 2011), relatively high concentration (i.e., about 2.0 ng/m^3) and deposition fluxes (i.e., 50 $g/m^2/year$) were found in many places in Asia including the Northern region of Thailand. This fact raises questions on the potential of national emission sources, and their contribution of emission inflow / outflow to Hg deposition in Thailand. In this regard, the understanding of several factors, such as source characteristics, meteorological conditions and chemical transformation, is required.

1.3. Research Objectives

1) To investigate and to assess Hg emissions sources in Thailand,
2) To characterize Hg deposition in Thailand, and
3) To investigate Hg inflow and outflow to and from Thailand, respectively.

1.4. Scope of Work

1) Hg emission sources include anthropogenic and natural sources within Thailand.
2) Assessment of the seasonal variation of Hg deposition and of the sensitivity of the deposition to Hg emission changes is conducted using AQ model,
3) Annual outflow of Thailand’s emissions to the global pool is also investigated using the AQ model
4) CAMx is the AQ model used in this study.

1.5. Overall Research Framework

Methodology of the work is described in Figure 1.4 to fulfill the objective set in this work including (1) Hg emissions characterization, (2) Hg deposition, and (3) Hg emissions inflow and outflow to and from Thailand.

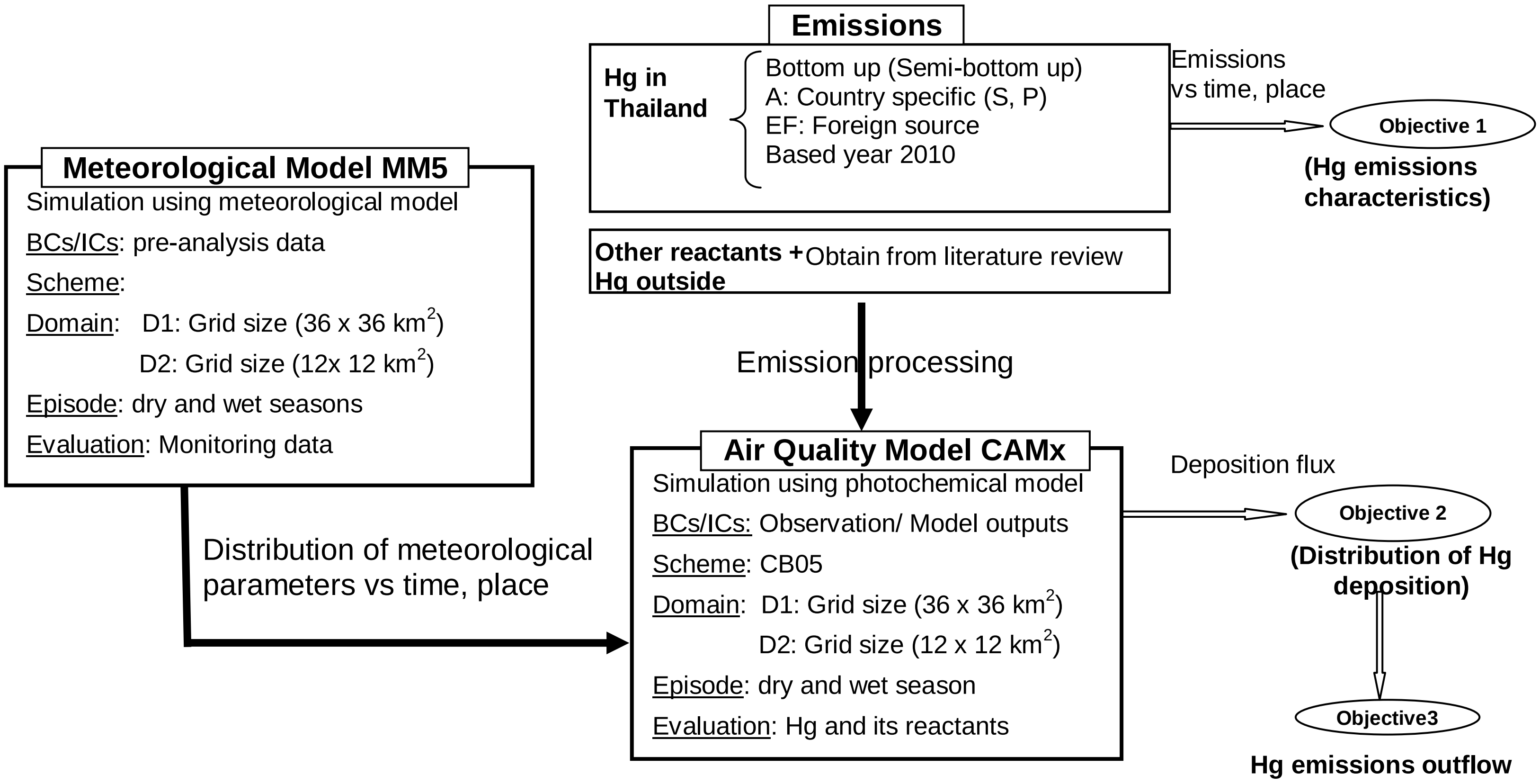


Figure 1.3: Schematic Diagram of the Work

CHAPTER 2

CHARACTERIZATION OF ATMOSPHERIC MERCURY

This chapter provides up-to-date literature review, theories/approaches and the background of Hg studies, including the fate of Hg in the atmosphere from emissions to deposition.

To assess Hg risk to humans and ecosystems, knowledge of Hg emissions characteristics, transportation and transformation is required. In the simplest approach, the concentration of chemical species in the atmosphere is governed by four main processes:

- Emissions: Chemical species are emitted in to the atmosphere by a variety of sources. They include emissions from natural sources and anthropogenic sources.
- Transformation: Chemical reactions in the atmosphere can lead to the transformation and removal of species. (e.g. through wet or dry deposition).
- Transportation: Winds carry atmospheric species away from their point of emission to other receptor areas.
- Deposition: All materials in the atmosphere are eventually deposited back on to the Earth's surface. Deposition includes (a) dry deposition: involving direct reaction or absorption at the Earth's surface and (b) wet deposition: involving scavenging by precipitation.

Figure 2.1 below presents in brief the cycles of Hg including emissions, chemical reaction, transportation and deposition in a modeling perspective.

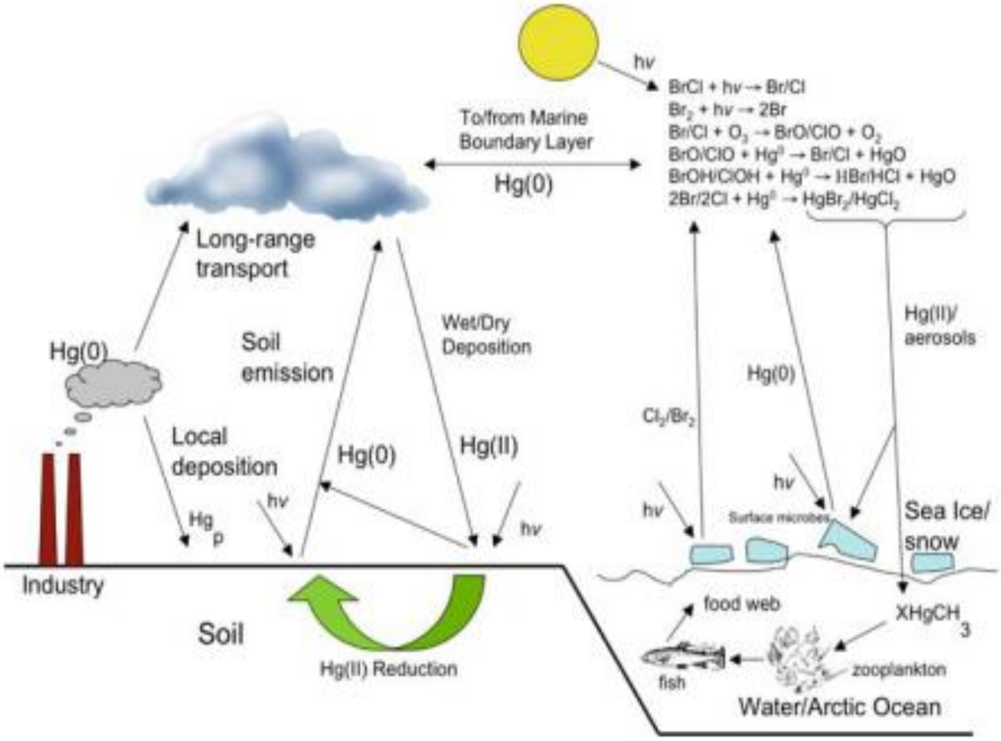


Figure 2.1: Hg Transformation in the Atmosphere (Ariya *et al.*, 2009)

As seen in Figure 2.1 above, Hg is emitted from both anthropogenic and natural sources. In the existing of other species as Hg reactants in the atmosphere (from both anthropogenic and natural sources), under condition of sunlight, several chemical reactions are happened. At the same time, wind parameters influence transportation of air mass (which consists of emissions and concentration of different species). Under appropriate condition, wet or dry depositions are happened as removal phenomenon of concentration. Once deposited to earth surfaces (i.e., water or soil), Hg emissions can be re-emitted through natural processes.

The following section, reviews of each of the 4 processes mentioned above: emissions by emissions inventory, transportation by meteorological model, transformation and deposition by air quality model are discussed.

2.1. Atmospheric Hg

2.1.1. Atmospheric Hg Emission Sources

Hg atmospheric emissions include both natural and anthropogenic (man-made) sources. While natural emissions sources have been quite stable for many decades, anthropogenic emissions are increasing due to increasing combustion and industrial activity to serve human demand. Present potential sources of atmospheric Hg emissions are defined below.

2.1.1.1. Natural Sources

a) Volcanoes and Geothermal Activity

Hg element originates from the Earth's crust and its emissions can be released during degassing or the eruption phase of volcanoes as well as from geothermal activity (e.g. hot springs, boiling mud pools). In general, Hg emissions from these sources are emitted in the form of gaseous Hg^0. To estimate Hg emissions, the ratio of Hg/SO_2 is applied instead. In average, volcanoes and geothermal activities contribute Hg into the atmosphere ~ 90 Mg / year (Pirrone *et al.*, 2009), which is responsible for approximately less than 2% of the total natural sources. By the nature of volcano activity, emissions of this source should be treated as episodic and elevated point sources.

b) Water Surfaces

Several studies suggest that the evasion of Hg from surface waters is primarily driven by (1) the concentration gradient of Hg between top-water micro-layer and air above the surface water, (2) solar irradiation, which is responsible for the photo-reduction of oxidized Hg in the top-water micro-layer and (3) the temperature of the top-water micro-layer and air above the surface water (air-water interface) (Pirrone *et al.*, 2009). The evasion of Hg from lake surfaces is generally higher than that observed over the sea. Global Hg emissions from water surface (including sea surface) are 2778 Mg, account for 53% of total natural Hg emissions (Pirrone *et al.*, 2009). Temporal distribution of this emissions source follows the pattern of ambient temperature (i.e., more emissions fluxes were recorded in the summer than winter) and it generally assumes that emissions occur only in summer and during the daytime (Wang *et al.*, 2006). This source is treated as an area source.

c) Soil Surfaces

Hg emissions from the soil surface are influenced by geo-terrestrial and meteorological factors. Emissions from soil surface include emissions from vegetable lands and forest and grassland etc. Global Hg emissions from soil surface are approximately 1,646 Mg, account for 31% of total natural Hg emissions (Pirrone *et al.*, 2009). Similar to those of water surfaces emissions, temporal distribution of soil surface emissions are following temperature ambient air and the same assumption (i.e., emissions are emitted only during summer and daytime are generally made). This source is treated as area source.

2.1.1.2. Anthropogenic Sources

a) Stationary Combustion

Hg emissions from combustion sources are caused by Hg content in fossil fuels and released unintentionally during combustion processes. Hg content is generally highest in coal (i.e. 0.01 – 0.48 mg/kg), followed by biomass and oil. It is of note that natural gas may contain small amounts of Hg but the element is normally removed from the condensate gas during the recovery of liquid constituents as well as during the removal of undesirable hydrogen sulfide. Therefore, it could be assumed that Hg emissions during the natural gas combustion are insignificant (Pirrone *et al.*, 2009) and it has not been included in any regional or global estimates. While total Hg emissions are strongly influenced by Hg content in fuel, their speciation (i.e. fraction of Hg^0, Hg^{2+}, and Hg^P) are varied by other oxidant substances in fuel (i.e. Clorine - Cl_2), boiler configuration, combustion conditions, and Air Pollution Control Devices (APCDs) (Lee *et al.*, 2004; Lei *et al.*, 2007; Tang *et al.*, 2007).

b) Non-combustion Processes

Cement Production

Hg emissions from cement production are caused by Hg content in raw materials (i.e. limestone). In addition, cement industry obtain recycled streams such as bottom ash from power generation. A significant fraction of the Hg present in the feed is not retained in the cement product but release as solid (which can be collected in the particulate air pollution control system) or gas, causing atmospheric Hg emissions (Pirrone *et al.*, 2009).

Mining and other Metallurgic Activities

Mercury Mining

The evaluation of global primary Hg production is very uncertain because most countries do not report their Hg production in their official statistical yearbooks. Current Hg production on annual basis shows that nearly 1800 Mg of Hg was produced in 2000, mainly from China and Kyrgyzstan (Pirrone *et al.*, 2009).

Iron-Steel Manufacturing

Steel is an alloy of iron and carbon. It is produced in a two-stage process. First, molten iron, which is either cast into pig iron or carried to the next stage as molten iron, is produced with coke and limestone in a blast furnace. In the second stage, molten still iron is produced by removing impurities such as sulfur, phosphorus, and excess carbon and adding alloying elements such as manganese, nickel, chromium and vanadium. Hg emitted mostly from impurity of input material (i.e., in iron ore), and of combustion processes (i.e., coke, limestone, exceed air) (Pirrone *et al.*, 2009).

Non-ferrous Metal Manufacturing

Hg has been found in trace elements in the most non-ferrous ores, such as zinc, copper, lead, gold, and silver. Hg emitted mostly from impurity of input material and smelting process. Hg emissions from the non-ferrous metals both primary and secondary refining processes are considered as significance (about 310 Mg in the year 2007 (Pirrone *et al.*, 2009).

Atisanal Gold Mining

Hg is used in artisanal gold mining activities for enhancing gold extraction. It is becoming one of the most prominent environmental and human health issues with Hg emissions discharged with tailings and/or volatilized into the atmosphere. Almost all activities have taken place in developing countries and countries with economies in transition where adverse environmental and health effects during the processes are not considered (Pirrone *et al.*, 2009).

Mercury Extraction

Pure Hg is extracted from ore, cinnabar, and Hg sulphide (HgS) for use in many industries. The process is that cinnabar ore is grinded to reduce the size, and heated. As a consequence, due to its relatively low boiling point, Hg condensing in cinnabar can be easily purified by using a vacuum distillation method (Pirrone *et al.*, 2009).

Caustic Soda Production (Chlor-alkali Plants)

Caustic soda, or Sodium Hydroxide (NaOH), is used in the chemical industry (i.e. alkaline-based manufacturer such as pulp and paper, textiles, soaps, detergents, and chlorine production). The most conventional process to produce caustic soda is Hg cell process which is also called the Castner-Kellner process. By using this process, Sodium ions (Na^+) are formulated to sodium metal of amalgam in an Hg cathode side and reacted with water (H_2O) to produce NaOH. Nowadays, caustic soda plants are encouraged to shift from Hg cell technology to Hg-free ones such as membrane cell or diaphragm cell (Pirrone *et al.*, 2009).

Manufacturing of Products Containing Hg

There are several kinds of Hg containing products used in daily life, such as batteries, fluorescent bulbs, medical instruments, dental amalgams, and cosmetics. Due to human health concern in Hg toxics, national federal agencies and governmental environments are in charge to reduce the cutting back or to eliminate Hg in such products to environment.

For example, **a battery or a Hg oxide battery** is a kind of non-rechargeable electrochemical battery with primary cells of positive and negative poles. It is a main power source of many electrical types of equipment for a daily life ranging from 0.5-10 voltage. It is cheap with varieties to fit in many products, and easily ordered or found in local markets. Thus, it becomes widely popular. Battery cathode has a very flat discharge curve holding constant power for open circuit voltage until eventually the last 1-5% of their lifetime. When their voltage drops and causes a malfunction to the electrical equipment, owners always dispose and replace the new battery. This tends to have very high risk for Hg-contaminated garbage as the result of a ban in many countries. Recently, a rechargeable battery offers the benefits to extend the lifetime while a non-Hg battery with longer lifetime has been more used instead.

Fluorescent bulbs are another product that is widely used. A gas-discharge lamp inside the tube requires electricity to energize Hg vapor in the excitation stage. The excited Hg ions produce ultraviolet light to enlighten a phosphor to fluoresce in the tube and shining a visible light. Ballast will then automate to regulate the flow of electricity current and maintain the flux of light stream. Fluorescent bulb consumes electrical power in a more useful and efficient manner with longer lifetime than classical oil-burning lamp. However, similar problem of vaporous Hg in fluorescent garbage has still been an issue unless the awareness on disposal management is carried on.

Thermometers have been widely used in measuring temperature, particularly in human body to determine the degree of sickness. Hg-based thermometer is then become the first aid tool commonly available in hospitals or at home. Nowadays thermometers use more pigmented alcohol or replace electric circuit instead of Hg. However, they are still used in medical research because of its accuracy and reliability.

Dental fillings use Hg amalgams to cure rotten teeth. Hg-used amalgam is acceptable safety even a person chews, swallows, drinks or breathes, Hg vapor cannot expose or release from dental fillings to absorb by lungs under the normal condition and use of mouth. In addition, as they corrode, Hg fillings release very little ionized Hg into the saliva, tooth pulp, and gum tissues leading to the digestive system and bloodstream, which is no harm at all. However, it will become an issue of atmospheric Hg if burnt human body in crematoria without this awareness.

Landfills

Municipal landfills contain many Hg-contaminated products, such as electrical switches, fluorescent bulbs, thermometers, etc. During the processes (collection containers, transport vehicles, and transfer stations, waste handling operations), Hg can release and evaporate to the atmosphere. Especially, once deposited, Hg can be converted to CH_3Hg under the presence of bacteria (United Nation Environment Programme, 2011).

c) Mobile Combustion Sources

Hg emissions from mobile sources are from the combustion of fuels containing Hg (e.g., gasoline, diesel, and liquefied petroleum gas (LPG)). Though Hg emission factor from mobile emissions are quantitatively reported (Won *et al.*, 2007), Hg emissions are mostly neglected in regional/ national Hg emission inventory due to the relatively small compared to many other categories (US-EPA, 1997).

2.1.1.3. Re-emissions Sources

Re-emission sources of Hg can be considered as natural or anthropogenic, though mostly the former, depending on the cause of emissions. Source of re-emissions Hg are naturally caused forest fire, air-surface exchange (ocean, lake, soil), and manmade forest fires and agricultural burning. Primary sources of re-emissions can be direct from landfills or indirect from wet and dry deposition. The amount of re-emissions from deposited sources depends on other factors such as releasing surfaces, weather condition and chemical reaction.

Among re-emission sources, Hg from biomass burning can be significant depending on the Hg content in the biomass. Biomass burning emissions are somewhat controversial that they can be either classified as natural or anthropogenic emissions. Global Hg emissions from biomass burning are estimated as 675 Mg in base year 2008 (Pirrone *et al.*, 2009). Customarily, location of burning area is derived from satellite image and presented as pixel. It is reasonable to assume that areas bunt equal the resolution of pixel. Biomass emissions can be treated as point or area. Biomass emissions can be episodic, normally happen in dry season (accidentally or naturally) or during harvesting period (intentionally by manmade).

2.1.2. Hg Emissions Estimates

2.1.2.1. Methodology of Atmospheric Hg Emission Estimates

Customarily, the magnitude of the emissions of a species is a function of the emitted process which defined by the emissions factor, which is the intensity of processes surrogated by activity data.

There are in general two approaches for inventory development (i.e., top-down and bottom-up approaches). The top-down approach derives emission estimates from national- or regional-scale data. The top-down approach widely has been widely used in many cases (e.g. regional or global estimates) because it requires less-detailed data. The bottom-up approach uses site-specific data of individual sources and sums all results for a national or regional level. The bottom-up approach has better accuracy than the top-down approach because the data are collected directly from individual sources. There are several methods for emission inventory depending on resources available and purpose of use. Figure 2.2 below presents the methods listed by the US EPA (United State Environmental Pollution Agency, cited 2006). As seen, more reliable but higher cost are within the group of analyzing, sampling and monitoring for source specific, especially, Continuous Emissions Monitoring Systems (CEMS), which provide hourly emissions at stack, is best desired but not often available due to high cost of installation and maintenance. These methods are suitable for estimating emissions of a single source for purpose of policy makers ‘decision. In contrast, less reliable are within the group of using adopted data and assumption in condition that similar of technology, fuel composition etc. These approaches are common for estimating emissions in large scale where sampling or monitoring is limited. Customarily, estimating emissions of multi-sources in regional/national/global scale, the use of EFs approach together with expert judgment are appropriate where it is compromise the uncertainties and the cost.

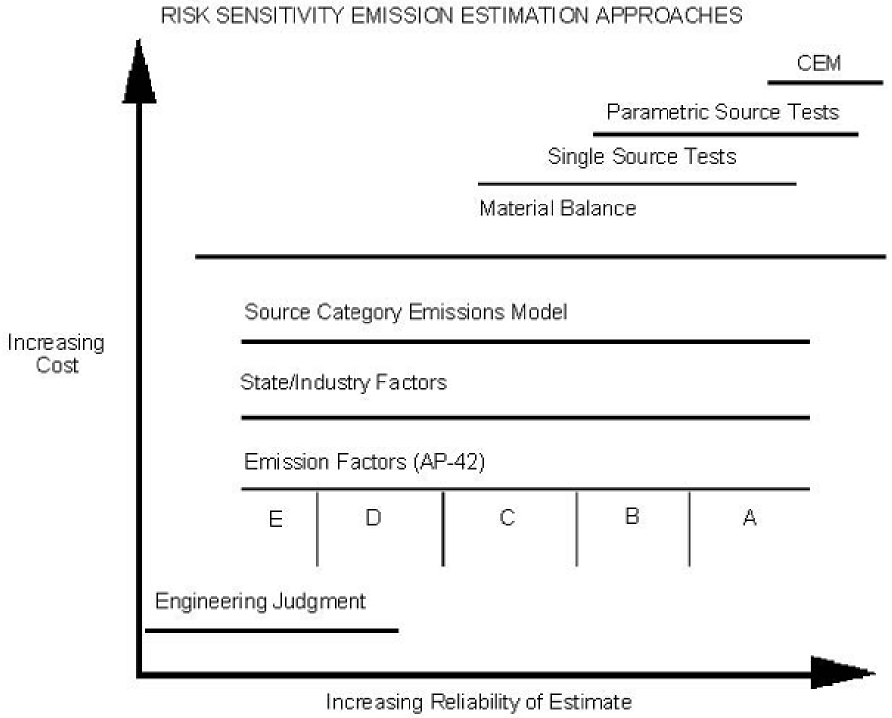


Figure 2.2: Approach to Emission Estimation (United State Environmental Pollution Agency, cited 2006)

2.1.2.2. Review of Global Hg Emission Inventory

In the past decades, Hg emission inventory was conducted on several levels, including global, regional and local scales. Each of them has different approach varying on level of detailed data. While global, regional EI in generally use top-down approach, sub-regional or local EI often use bottom-up approach or mixture of top-down and bottom-up approach, a so called semi-bottom up approach. In section below, available EIs in global, regional and local levels are reviewed.

There has been global concern about Hg during the last few decades. Global emissions are useful in providing information on emissions situation in global scale as well as serve as global model input. Main methodology used in global estimates is top down approach using statistical data and best suitable EFs. In Table 2.1a, where global natural and anthropogenic emissions (obtained from (Pirrone *et al.*, 2001)) are presented, emissions from natural sources are dominant and as twice as those from anthropogenic sources. Within natural Hg emissions, emissions from ocean sources are dominant (account up to 50%), follow by those from soil surface (in sum account up to 31%), and biomass burning (13%). Within anthropogenic sources, Hg emissions from coal and oil combustion are dominant with 50% share, following by emissions from artisanal gold mining and non-ferrous metal industries (i.e., 13.8% and 10.7 %, respectively).

Table 2.1:(a) Global Atmospheric Hg Emissions from Both Natural and Anthropogenic Sources (Pirrone *et al.*, 2009)

Emission Source	**Hg Emissions (Mg/yr)**	**Reference Year**
Natural		
Ocean	2,682	2008
Lakes	96	2008
Forest	342	2008
Tundra/Grassland/Savannah/Prairie/Chaparral	448	2008
Desert/Metalliferrous/Non-vegetated zones	546	2008
Agricultural areas	128	2008
Evasion after Hg depletion events	200	2008
Biomass burning	675	2008
Volcanoes and geothermal areas	90	2008
Total (Natural)	*5,207*	
Anthropogenic		
Coal combustion, oil combustion	1,422	2000
Pig iron and steel production	43	2000
Non-ferrous metal production	310	2007
Caustic soda production	163	2000
Cement production	236	2000
Coal bed fires	32	2007
Waste disposal	187	2007
Mercury production	50	2007
Artisanal gold mining production	400	2007
Other	65	2007
Total (Anthropogenic)	*2,909*	
Total (Natural +Anthropogenic)	8,116	

Hg emissions by country during year 2005 were developed for the whole world. The detailed approach and results can be found in the AMAP technical reports (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). For some countries where national estimates were available in bottom up approach, the estimates were directly adapted whereas for others, where neither national estimates and country specific bottom data were available, top down approach was chosen utilizing international statistics and adapted/adopted EFs. Details of the estimates in low-end and high-end estimate are shown in Table 2.1b. As seen, the uncertainties of global atmospheric Hg from anthropogenic sources are approximately in factor of 2 (or 135%). Each source has uncertainties from ±25% to ±30%, except that Hg emissions from waste incineration sources have highest uncertainties as much as 5 times.

Table 2.1 (b): Global Atmospheric Hg Emissions from Anthropogenic Sources (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

Sector	**Emissions of Year 2005 (Mg/yr)**		
	Mean (Percentage)	**Low-end**	**High-end**
Fossil fuel combustion for power and heating	878 (45.5)	595	1160
Metal production	200 (10.4)	123	276
Large-scale gold production	111 (5.8)	66	156
Artisanal and small-scale gold production	351 (18.2)	225	475
Cement production	189 (9.8)	114	263
Chlor-alkali industry	47 (2.4)	29	64
Waste incineration, waste and other	125 (6.5)	53	473
Dental amalgam application	25.7 (1.3)	24	28
Total	1,930 (100)	1,229	2,895

Released in year 2013, AMAP/UNEP (Wilson, 2013) provided global emission 2010 atmospheric Hg gridded database with gridded resolution being 0.5deg. Emissions vertical distribution is in 3 levels (i.e., 0-50m; 50 - 150m and higher than 150m) are presented in Table 2.2. Among speciation, Hg^0 emissions are dominant, accounted for 81.4% and Hg^{2+}

and Hg^P accounted for 14.6% and 4%. Among 3 levels, major Hg emissions are within level 50 m (with 54.8%), 28.2% of atmospheric emissions are in 50m – 150m, and 17.1% of atmospheric emissions are released beyond 150m.

Table 2.2: Vertical Distribution of Global Atmospheric Hg Emissions (Wilson, 2013)

Released Height	**Emissions (Mg)**			
Species	**0 m - 50 m**	**50 m - 150 m**	**> 150 m**	**Total**
Hg^0	943	423	162	1,527
Hg^{2+}	68	79	127	274
Hg^P	17	26	32	75
Total	1,027	528	320	1,875

In Figure 2.3 below, spatial distributions of Hg emissions by species are presented. The emissions were mostly located in the Asian region, especially India and the eastern part of China.

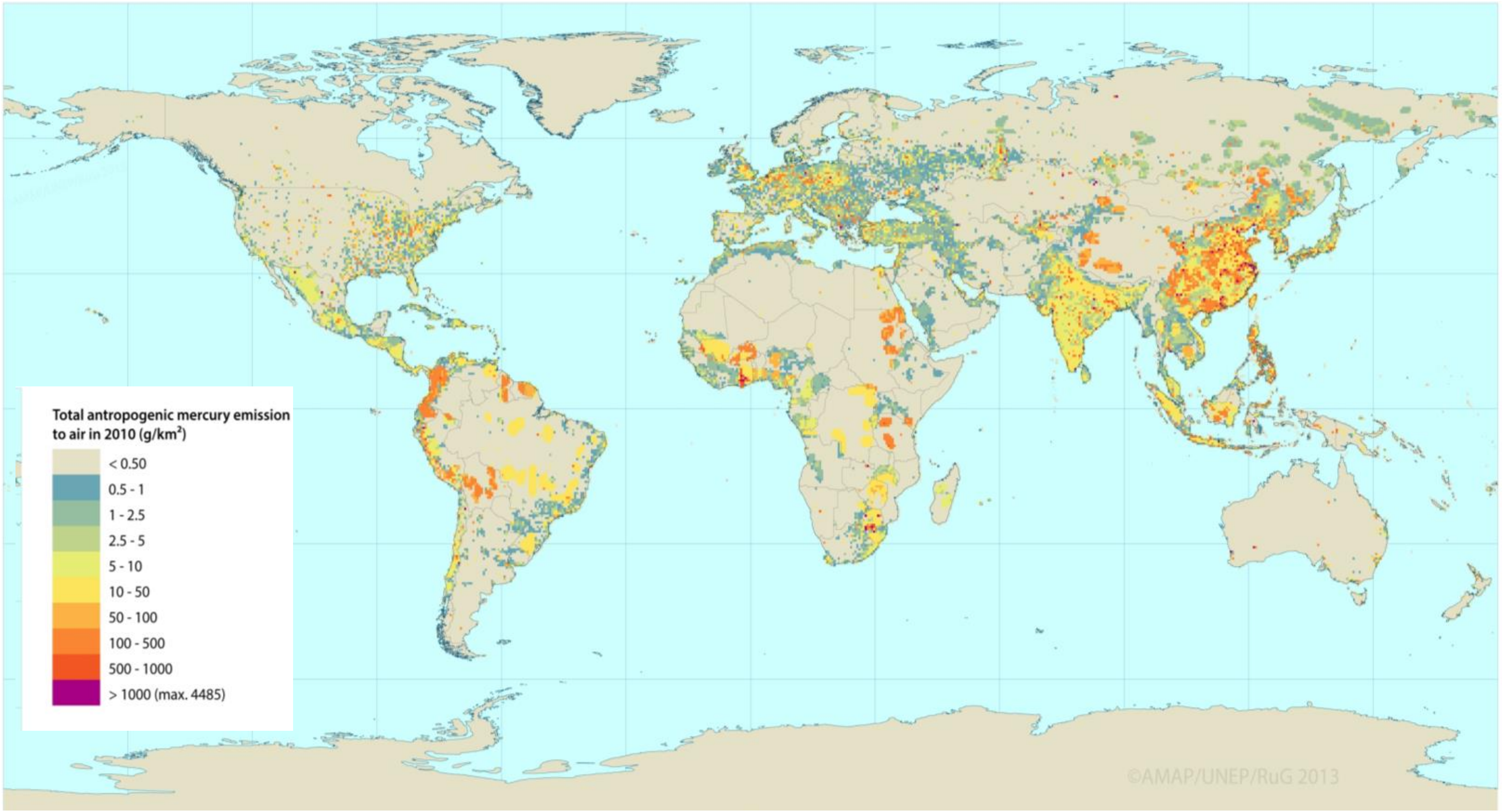
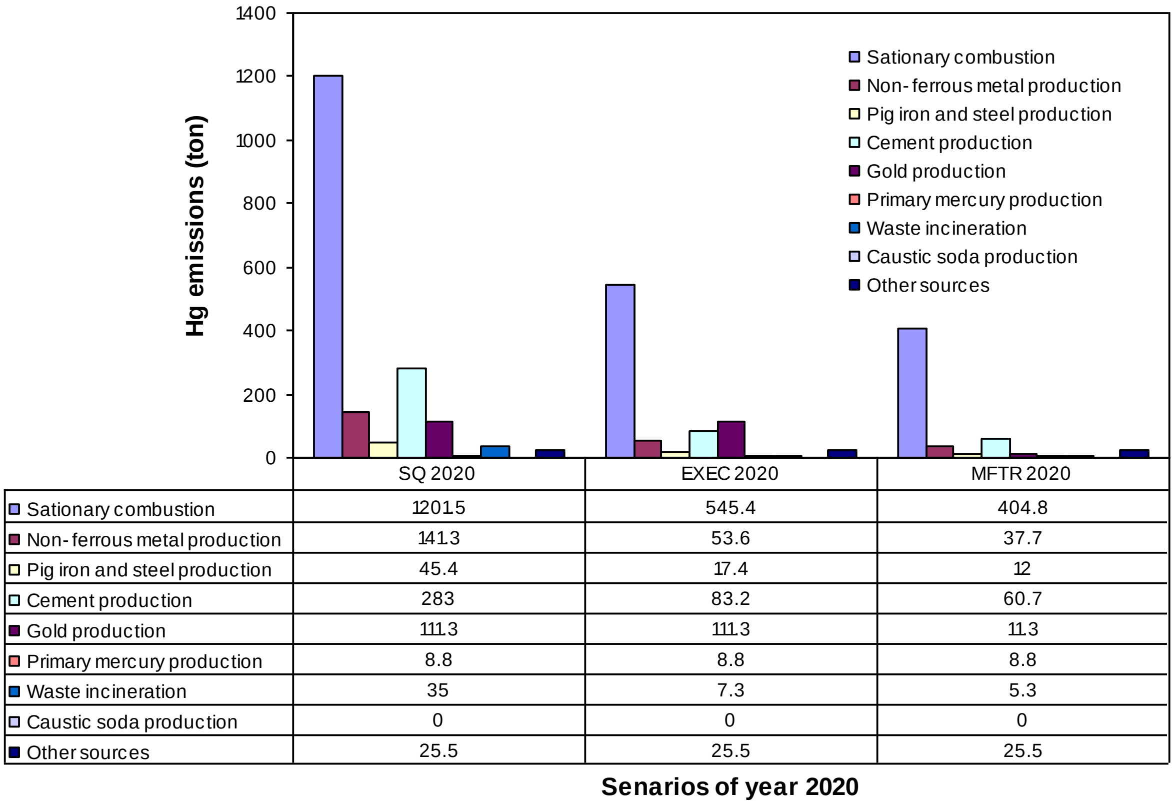


Figure 2.3: Spatial Distribution of Total Atmospheric Hg Emissions from Anthropogenic Sources in Year 2010 (Wilson, 2013)

Beside the above works, global Hg emissions were recently estimated using a combination of bottom-up and top-down method (Streets *et al.*, 2009). Emissions were estimated for year 2006 and projected to year 2050 under a variety of assumptions about socioeconomic and technology development, following patterns of energy and fuel use under alternative IPCC scenarios (Nakicenovic, 2000). Compared to 2006 levels of 2,480 Mg, 2050 global Hg emissions were projected to be 2,390 - 4,860 Mg, corresponding to a change of -4% to+96%. In general, global emissions in year 2050 are likely to increase, mostly driven by the expansion of coal-fired electricity generation in the developing world, particularly Asia.

In Figure 2.4 below, the projection of global atmospheric Hg emissions in the year 2020 were extracted from the literature (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). Emissions projections are assessed for 3 scenarios: SQ 2020, EXEC 2020 and MFTR 2020 for which Hg emissions were estimated as follows: 1,851.8 Mg, 852.5 Mg and 566.1 Mg, respectively. Compared to SQ 2020, emissions in the case of EXEC were reduced 54% and MFTR were reduced 69.4% and large reduction was found mostly in the case of stationary combustion and production, such as non-ferrous metal production and cement production.



	SQ 2020	EXEC 2020	MFTR 2020
Sationary combustion	1201.5	545.4	404.8
Non- ferrous metal production	141.3	53.6	37.7
Pig iron and steel production	45.4	17.4	12
Cement production	283	83.2	60.7
Gold production	111.3	111.3	11.3
Primary mercury production	8.8	8.8	8.8
Waste incineration	35	7.3	5.3
Caustic soda production	0	0	0
Other sources	25.5	25.5	25.5

a) SQ: Status Quo, where current patterns, practices and uses continue. Economic activity increases but emissions control practices remain unchanged.

b) Exec: Extended Emissions Control, where emissions control technologies currently used in Europe and the USA are used elsewhere (such as those required under LRTAP conventions, EU directives and so on). This would include control technologies such as ESP or bag houses and FGD systems on coal combustion systems.

c) MFTR: Maximum Feasible Technology Reduction, where all available solutions/measures are implemented leading to maximum mercury reduction with cost being a secondary consideration. This would mean the use of activated carbon injection (ACI) and other similar sorbent-based systems.

Figure 2.4: Projection of Global Atmospheric Hg Emissions until Year 2020 (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

2.1.2.3. Review of Regional Hg Emissions Inventory

In this section, the regional estimation of atmospheric Hg is presented in Table 2.3 for Africa, Asia, Europe, North America, Oceania, Russia, and South America according to the estimate of AMAP/UNEP (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). As seen, Asia share highest contribution to global emissions with 66.5% followed North America and Europe with 7.9% and 7.8% respectively. Fossil fuel combustion for power and heating had large contribution for all regions (especially for Asia, North America and Europe), and artisanal and small-scale gold production also contribution to Asia and South America. Uncertainties of the estimates are ±27 to ±50% with the highest uncertainties in Africa.

Table 2.3: Atmospheric Hg Emissions by Region (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

Region	**Emissions of Year 2000 (Mg/yr)**		
	Mean (Percentage)	**Low-end**	**High-end**
Asia	1,280 (66.5)	835	1760
North America	153 (7.94)	91.4	305
Europe	150 (7.78)	90.8	309
South America	133 (6.9)	82.0	196
Africa	95.4 (5.0)	57.6	141
Russia	73.9 (3.8)	44.6	132
Oceania	39.1 (2.0)	28.2	50.0
Total	1,930	1,230	2,893

The section following presents 10 countries with the highest atmospheric Hg emissions. Their combined atmospheric Hg emissions account for 74.3% of total global atmospheric emissions. Among the ten countries listed in Table 2.4, China and India share the largest contributions. Together, they contributed more than 50% of total global estimates.

Table 2.4: 10 Countries with Highest Atmospheric Hg Emissions (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

Country	**Emissions of Year 2000 (Mg/yr)**				
	Total (Percentage[a])	**Stationary Combustion**	**Industrial Production**	**Artisanal Gold**	**Other Sources**
China	825.2 (42.9)	387.4	243.2	156.0	38.6
India	171.9 (8.9)	139.7	21.6	0.5	10.1
USA	118.4 (6.2)	62.8	31.7	0.5	23.4
Russia	73.9 (3.8)	46.0	18.9	3.9	5.1
Indonesia	68.0 (3.5)	3.3	10.2	50.9	3.6
South Africa	43.1 (2.2)	33.4	5.7	2.6	1.4
Brazil	34.8 (1.8)	4.8	11.4	15.8	2.8
Australia	33.9 (1.8)	17.7	15.2	0.4	0.6
South Korea	32.2 (1.7)	18.1	12.9	0	1.2
Columbia	30.0 (1.6)	0.8	2.3	26.3	0.6
Total	1,431.4 (74.3)				

a) Percentage between the countries and the global emissions.

Table 2.5 shows the analysis of emissions estimation focusing on Asia. For inventory year 2000, Hg emissions from Asia were 1,280 Mg, which China and India have highest contribution with 64.7% and 16.5% respectively. Within Southeast Asia, Indonesia has the largest Hg emissions (accounted for 37.9%, mostly from large scale gold production, stationary combustion and cement production). Thailand is the second largest Hg emitter in Southeast Asia (SE) region, which accounted for 28.5% of total emissions. Hg emissions from Thailand were mostly from stationary combustion and cement production. Philippine and Vietnam have similar contribution to SE emissions, which account 15.3% and 15.5% of total, respectively. The other SE Asian countries share less contribution, which totally account for approximately 2.6% (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). Emissions per capita of 10th largest country emitter in SE Asia region shown in Table 2.5 figured that Malaysia and Thailand have highest capital emitters with 180.0 and 161.5 µg/person, respectively.

Table 2.5: Annual Hg Emissions, Population and Emissions Per Capita in Some SE Asian Countries for Year 2000

Country	**Hg Emissions (Mg/yr)[a] Magnitude (Percentage)**	**Population (million)[b]**	**Emissions/Capita (µg/person)**
Indonesia	13.4 (33.7)	225.5	59.3
Thailand	10.1 (25.4)	65.2	154.6
Vietnam	5.5 (13.8)	84.2	64.8
Philippines	5.1 (12.8)	86.3	62.8
Malaysia	4.8 (12.1)	26.9	177.2
Singapore	0.5 (1.3)	4.5	103.3
Laos	0.3 (0.8)	6.1	55.7
Myanmar	0.09 (0.2)	51	1.8
Brunei	0.02(0.1)	0.4	42.5
Cambodia	0.01 (0.0[c])	14.1	0.6
Total	39.82		

a) (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

b) Population recorded in midyear 2000 (Population Reference Bureau, 2006)

c) Less than 0.05

There were a number of EI works focused on the Asian region, which can be summarized as follows:

1) Bottom-up method for estimating atmospheric Hg emissions (Streets *et al.*, 2005)

2) Data assimilation and inverse modeling for estimating atmospheric Hg emissions (Pan *et al.*, 2007)

3) UNEP Toolkit approach to investigate the Hg budget in all pathways (i.e. air, water, soil, waste, and by-products) (Department of Environmental Pollution Control, 2008; Environmental Management Bureau, 2008)

4) Mass balance method through stack sampling to estimate Hg emissions for some specific sources (i.e. mostly combustion) (Lee *et al.*, 2006; Lei *et al.*, 2007). Those sampling papers provide good reference for not only understanding the transformation of Hg species in the combustion chamber under different boiler configurations, fuel type, combustion condition but also knowledge on emissions reductions of each combination of air pollution control devices (APCDs).

2.1.2.4. Hg Emissions Inventory of Thailand

Hg emissions in Thailand were first investigated by an international organization named Green Peace. They were concerned about hazardous metal contaminates in coal combusted facilities. Total three samples from two power generating facilities using coal as main fuel are collected and analyzed. The sampling results indicated that fly ashes are relatively highly contaminated with metal hazardous (e.g., As, Hg) (Green Peace, 2002).. However, due to limited numbers of facilities visited and samples collected (i.e., 3 samples were collected from 2 factories), the results may not representative and reflect the real emitting nature of the plants.

Another recent international effort that estimates anthropogenic Hg emissions for the globe, including Thailand, are from the Arctic Monitoring and Assessment Programme - United Nation Environment Program (AMAP/UNEP) with a and the based year in 2000 (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). It found that in year 2000, total anthropogenic Hg emissions in Thailand are 10.08 Mg, of which the largest contributions were from stationary combustion (up to 60%), and cement (up to 30%) as seen in Table 2.6. This estimate was useful to provide for inter-comparison for emissions from anthropogenic sources, however, it should be noted that this may be overestimated for some source such as combustion in thermal power plants and industrial facilities due to no taking account the local measurement of emission control efficiency and under-estimated due to not account some local sources (e.g., small to medium incinerators, unofficial gold mining using amalgam). The approach for its spatial distribution was mainly based on world population map which may not well reflect local source location. In addition, the estimates did not include biomass burning and natural emission sources.

Table 2.6: Mercury Emissions in Thailand (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

Sources	**Emissions (Mg/yr)**			
	2000	**2020_SQ**[a]	**2020_Exec**[b]	**2020_MTFR**[c]
Stationary Combustion	6.08	8.89	3.95	2.88
Non-ferrous Metal	0.58	0.58	0.21	0.15
Pig Iron and Crude Steel	0.21	0.21	0.08	0.06
Cement Production	3.03	4.55	1.33	0.97
Large-Scale Gold	0.18	0.18	0.18	0.18
Mercury Production Primary	0	0	0	0
Incineration Municipal Waste	0	0	0	0
Caustic Soda Production	0	0	0	0
Other	0	0	0	0
Total	10.08	14.40	5.74	4.24

a) SQ: Status Quo, where current patterns, practices and uses continue. Economic activity increases but emissions control practices remain unchanged.

b) Exec: Extended Emissions Control, where emissions control technologies currently used in Europe and the USA are used elsewhere (such as those required under LRTAP conventions, EU directives and so on). This would include control technologies, such as ESP or bag houses and FGD systems, on coal combustion systems.

c) MFTR: Maximum Feasible Technology Reduction, where all available solutions/measures are implemented leading to maximum mercury reduction with cost being a secondary consideration. This would mean the use of activated carbon injection (ACI) and other similar sorbent-based systems.

More locally, a study applied the UNEP Toolkit for estimating a series of annual Hg emissions in Thailand up to the year 2009 using a top-down approach. Emissions sources were classified into 10 main groups in which 4 major emitters are (1) extraction and use of fuels/energy sources, (2) primary (virgin) metal production, (3) other intentional products/process uses, and (4) Consumer products with intentional use of Hg. The approach was following top down, which national statistical data and UNEP default emission factors were used. Emissions of each pathway were allocated using distribution factor (to air, soil, water, and by product). Recommendation for Hg emission control management was also presented (Khongpaitoon, 2010).

Most recently, the Pollution Control Department (PCD) of Thailand conducted 2 projects involving Hg assessments from industrial facilities. The former started in 2009 investigated Hg and heavy metal emissions from industrial combustion by stack sampling method. Twenty one representative industrial facilities varying by boiler type, fuel used and air pollution control devices equipped were chosen. The later started in 2010 assess Hg emissions by stack sampling from 5 coal fuel boiler facilities. Both projects provided Hg concentrations at stack, emission control efficiencies as well as stack parameters, which customarily were key information to develop local emission factors. However, due to limited number of sampling, the stack information is used to indicate status of combustion processes, but cannot use to develop emission factor. In addition, projects presented to the community the contaminated levels of Hg and heavy metals and serve for policy makers as a guideline for preparing standard for controlling Hg and other heavy metal from industrial stacks (Pollution Control Department, 2010).

Another PCD project on Hg emissions inventory follows UNEP Toolkit approach including all pathways of air, water, waste, and land. In year 2010, Hg emissions to the environment in year 2010 were in range of 32,008.9 kg to 527,862.2 kg and uncertainties were mainly due to Hg content in fuel. For the lower range (i.e., total Hg emissions were 32,008.9 kg), Hg emissions were released to the environment as follows: air (34.2%), water (13.2%), soil (24.1%), impurities products (6.8%), general waste (16.6%), and sector specific treatment/disposal (5.1%). According to this study, within air pathway, extraction and use of fuels/energy sources and waste incinerator, consumption of Hg containing products and industrial processes were key emitters (accounted of 40.3%, 46.1%, 6.2% and 5.7% of total Hg emissions to air pathways).

2.1.3. Air Mass Circulation

2.1.3.1. Transportation

Transportation is caused by two main phenomenon: (1) Molecular diffusion: the process by which molecules spread from areas of high concentration to areas of low concentration, and (2) Wind field is the main meteorological factors that affects dispersion are wind direction, wind speed and atmospheric turbulence. There are two types of air pollutant transport caused by wind from mechanical turbulence (diffusion) and advection. They are carried along with the time-averaged (hourly) mean wind flow.

2.1.3.2. Regional Patterns of Climate in Southeast Asia and Thailand

The climate of Thailand is under the influence of the monsoons i.e. southwest monsoon and northeast monsoon. The weather of Thailand therefore can be classified into three seasons: rainy or southwest monsoon season (mid-May to mid-October), winter or northeast monsoon season (mid-October to mid-February), and summer or pre monsoon season (mid-February to mid-May). The southwest monsoon which starts in May brings a stream of warm moist air from the Indian Ocean towards Thailand causing abundant rain over the country, especially the windward side of the mountains. The northeast monsoon which starts in October brings the cold and dry air from the anticyclone in China mainland over major parts of Thailand, especially the Northern and Northeastern Parts which is higher latitude areas. In the Southern Part, this monsoon causes mild weather and abundant rain along the eastern coast.

Local wind is also important for a specific region or special area. In Thailand, the coastal areas of many provinces (e.g., Samutprakarn, Chachengsao, Chonburi) are highly influenced by local sea-land breeze from the Gulf of Thailand. According to climatologically data (i.e., mean temperature, and accumulate precipitation and number of rainy days of all 54 Thai Meteorological Department stations for year 2010, mean temperature in Thailand is from 25^{o} C to 35^{o} C and April and December are warmest and mildest months, respectively. The monthly accumulated precipitation is relatively high during May-October and highest in August while it is relatively low during November-February and lowest in February. The number of rainy days is in trends with monthly accumulated precipitation.

2.1.4. Chemical Transformation

2.1.4.1. Scientific Understanding of Hg Transformation in the Atmosphere

In the atmosphere, Hg exists in the form of elemental mercury (Hg^0), reactive gas or oxidized mercury (Hg^{2+}) in inorganic forms (i.e. mercuric chloride, $HgCl_2$) or organic forms (i.e., methyl mercury, CH_3Hg). Hg can exist as particulate mercury (Hg^P) (i.e. mercuric oxide (HgO) or mercury sulfide (HgS)). Hg^0 has a long lifetime in the atmosphere for several months. In contrast, Hg^{2+} and Hg^{P} have short atmospheric lifetime (few hours to few days) because they are greatly soluble so that can they can be removed shortly by wet or dry deposition (Lin and Pehkonen, 1999; Hynes *et al.*, 2009).

In the following section, a scientific understanding of Hg chemistry, which can be grouped into gas, aqueous, particulate matter, and equilibrium phases, is presented.

Gas Phase Reactions

Gas phase reactions involving Hg^0 are considered for 3 processes: (i) oxidation to HgO; (ii) oxidation to halogen compounds; (iii) reduction of Hg^{2+} to Hg^0.

Table 2.7: Hg Gas Phase Reactions (Pongprueksa, 2006 and references therein)

Reaction	**Rate constant ($cm^3 molec^{-1} s^{-1}$)**
$Hg^0(g) + O_3(g) \rightarrow HgO(s,g) + O_2(g)$	$3\text{-}490 \times 10^{-20}$
$Hg^0(g) + OH^\bullet(g) \rightarrow Hg^{2+} + \Pr oducts$	$8.7\text{-}12 \times 10^{-14}$
$Hg^0(g) + H_2O_2(g) \rightarrow Hg^{2+} + \Pr oducts$	8.9×10^{-19}
$Hg^0(g) + Cl_2(g) \rightarrow Hg^{2+} + \Pr oducts$	$1.82 – 26 \times 10^{-19}$
$Hg^0(g) + Br_2(g) \rightarrow Hg^{2+} + \Pr oducts$	$<9 \times 10^{-17}$
$Hg^0(g) + Cl(g) \rightarrow Hg^{2+} + \Pr oducts$	$7.6 – 100 \times 10^{-13}$
$Hg^0(g) + Br(g) \rightarrow Hg^{2+} + \Pr oducts$	3.2×10^{-12}
$Hg^0_{(g)} + BrO_{(g)} \rightarrow Hg^{2+} + \Pr oducts$	$10^{-13}\text{-}10^{-15}$

Aqueous Phase Reactions

In the atmospheric environment, aqueous phase reactions can occur in cloud-, fog- or rain-water and in films of moisture associated with hygroscopic aerosols. Hg-related aqueous-phase chemistry involves the reduction of Hg^{2+} to Hg^0 by using reactions with hydroperoxy radicals (HO^2) and by the formation of the sulfite complexes (at low HCl concentrations), $HgSO_3$ and $Hg(SO_3)_2^{2-}$, as well as the oxidation of Hg^0 to Hg^{2+} by dissolved O_3, OH, and Cl_2.

Table 2.8: Hg Aqueous Phase Reactions (Pongprueksa, 2006 and references therein)

Reaction	**Rate**
$HgSO_3(aq) \rightarrow Hg^0(aq) + S(VI)$	T exp(31.971T-12595)/T s^{-1}
$Hg(SO_3)_2^{2-}(aq) \rightarrow Hg^0(aq) + S(VI)$	<< 10^{-4} s^{-1}
$Hg(OH)_2(aq) + UV \rightarrow Hg^0(aq) + \mathrm{Pr}oducts$	3 x 10^{-7}, midday 60^{o}N
$Hg^{2+}(aq) + HO_2^{\bullet}(aq) \rightarrow Hg^0(aq) + \mathrm{Pr}oducts$	1.7 x 10^{4} M^{-1} s^{-1}
$Hg^0(aq) + O_3(aq) \rightarrow Hg^{+2}(aq) + \mathrm{Pr}oducts$	4.7 x 10^{7} M^{-1} s^{-1}
$Hg^0(aq) + OH^{\bullet}(aq) \rightarrow Hg^{+2}(aq) + \mathrm{Pr}oducts$	2.0 x 10^{9} M^{-1} s^{-1}
$Hg^0(aq) + HOCl(aq) \rightarrow Hg^{+2}(aq) + Cl^{\bullet} + OH^{\bullet}$	2.09 x 10^{6} M^{-1} s^{-1}
$Hg^0(aq) + OCl^{\bullet}(aq) \rightarrow Hg^{+2}(aq) + Cl^{\bullet} + OH^{\bullet}$	1.99 x 10^{6} M^{-1} s^{-1}
$Hg^0(aq) + HOBr(aq) \rightarrow Hg^{+2}(aq) + Br^{\bullet} + OH^{\bullet}$	0.279 M^{-1} s^{-1}
$Hg^0(aq) + OBr^{\bullet}(aq) \rightarrow Hg^{+2}(aq) + Br^{\bullet} + OH^{\bullet}$	0.273 M^{-1} s^{-1}
$Hg^0(aq) + Br_2(aq) \rightarrow Hg^{+2}(aq) + 2Br^{\bullet}$	0.196 M^{-1} s^{-1}

Particulate Phase Reactions

There are some Hg species remaining in the atmosphere as Hg_P compounds such as HgO, HgS, $HgCl_2$, $HgSO_4$, $Hg(NO_3)_2$. Possible chemical reactions related to Hg_P include the reduction of HgO to Hg^0 by CO, SO_2, NO or the addition of water to form $Hg(OH)_2$. However, due to uncertainties of Hg particulate phase and the lack of reaction rate, transformation of Hg_P is not included in current modeling effort (Ariya *et al.*, 2009).

Equilibrium Equations

In the atmosphere, mercury can equilibrate among the gaseous, aqueous and solid phases. Below are chemical equilibria for calculating aqueous phase Hg^{2+} speciation (Smith and Martell, 2004).

Table 2.9: Hg Equilibrium Equations (Pongprueksa, 2006 and reference therein)

Equilibrium	**Log (K_{eq})**
$H_2O \cdot SO_2 \leftrightarrow H^+ + HSO_3^-$	-1.91
$HSO_3^- \leftrightarrow H^+ + SO_3^-$	-7.18
$H_2O \cdot CO_3 \leftrightarrow H^+ + HCO_3^-$	-6.35
$HCO_3^- \leftrightarrow H^+ + CO_3^-$	-10.33
$Hg^{2+} + OH^- \leftrightarrow Hg(OH)^+$	10.63
$Hg^{2+} + 2OH^- \leftrightarrow Hg(OH)_2$	22.24
$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3$	12.7
$Hg^{2+} + 2SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$	24.1
$Hg^{2+} + OH^- + Cl^- \leftrightarrow HgOHCl$	18.25
$Hg^{2+} + Cl^- \leftrightarrow HgCl^+$	7.30
$Hg^{2+} + 2Cl^- \leftrightarrow HgCl_2$	14.0
$Hg^{2+} + 3Cl^- \leftrightarrow HgCl_3^-$	15.0
$Hg^{2+} + 4Cl^- \leftrightarrow HgCl_4^{2-}$	15.6
$Hg^{2+} + Br^- \leftrightarrow HgBr^+$	9.07
$Hg^{2+} + 2Br^- \leftrightarrow HgBr_2$	17.27
$Hg^{2+} + 3Br^- \leftrightarrow HgBr_3^-$	19.7
$Hg^{2+} + 4Br^- \leftrightarrow HgBr_4^{2-}$	21.2
$Hg^{2+} + OH^- + Br^- \leftrightarrow HgOHBr$	19.7
$Hg^{2+} + CO_3^{2-} \leftrightarrow HgCO_3$	11.0
$Hg^{2+} + SO_4^{2-} \leftrightarrow HgSO_4$	1.34
$Hg^{2+} + 2SO_4^{2-} \leftrightarrow Hg(SO_4)^{2-}$	2.40
$Hg^{2+} + NO_3^- \leftrightarrow Hg(NO_3)^+$	0.11

Heterogeneous Reactions

Heterogeneous reactions have reactants in two or more phases due to the reaction from air to surface (soil, water, vegetables, etc) (Ariya *et al.*, 2009).

2.1.4.2. Hg Reactants

Chemical transformation of Hg is influenced by their reactant, which is described in the section above; therefore, it is important to identify the key Hg reactants. In modeling approach, number of Hg reactant can be varied (which can be shown in Tables 2.7 - 2.9). In general, Hg chemistry needs concentration of O_3, H_2O^2, OH, SO_2, HO_2, Cl_2, Br_2, HCl, and atmospheric particulate matter (PM). This section reviewed some key Hg's reactants.

Ozone (O_3)

Ozone naturally exists in the stratosphere layer to protect our earth from the UV sunlight. In contrast, O_3 in the tropospheric layer, especially near the ground, is an air pollutant that impacts human health and the environment. Tropospheric O_3 is a secondary pollutant, which is not directly released from sources but produced by the photochemical reactions of NOx and NMVOC under the presence of sunlight. In addition, CO is a known reactor to enhance the O_3 production. NOx, NMVOCs, and CO are gaseous emissions that are highly produced and found in industrial and transportation activities, particularly in motor vehicles, petrochemical refineries, and power plants.

Hydroxyl Free Radical (OH)

The hydroxyl radical is one of the most important oxidants in the troposphere. It is a highly reactive and short-lived species. It is considered as "detergent" species and can react with many pollutants, including hydrocarbon and ozone.

Halogen

A halogen group, including Cl_2 or Br_2, is known reactants to oxidize Hg in both the gaseous and aqueous phases. Unfortunately, there is no comprehensive study on Cl_2 emissions inventory available from anthropogenic sources such as industries or businesses. Thus, some researchers applied natural Cl_2 production from sea salt instead (Bullock and Brehme, 2002; Environ International Corporation, 2011).

2.1.5. Deposition

Deposition is the process by which particles collect and deposit themselves. It can be divided into two sub-processes: dry and wet deposition. Wet deposition includes rain, fog, and cloud processes. It results from precipitation and cloud scavenging to clean the atmosphere. In wet deposition, there are always some atmospheric hydrometeors which scavenge aerosol particles. Dry deposition is gravitational coagulation with water droplets. Dry deposition is caused by one of the following reason: Gravitational sedimentation, interception, impaction, diffusion or Brownian motion, and turbulence.

2.1.5.1. Dry Deposition

Among its speciation, both Hg^{2+} and Hg^P are thought to be subject to much faster atmospheric removal than is Hg^0 (United State Environmental Pollution Agency, 1997; Lin and Pehkonen, 1999). Both Hg^{2+} and Hg^P are assumed to dry deposit at significant rates, which deposition velocity of Hg^P is dependent on atmospheric conditions and particle size while Hg^{2+} is dependent on its reactivity with surface material. Dry deposition flux of a species is a function of dry deposition velocity and the gaseous concentration of mercury species (Lin *et al.*, 2006)

$$F_{dry} = V_d \times C_g$$

Where

F_{dry} : Dry deposition flux (µg m^{-2} s^{-1})

V_d : Dry deposition velocity (m s^{-1})

C_g : Gaseous concentration (µg m^{-3}) of mercury species (i.e., GEM, RGM, or PHg)

Dry deposition velocity can be mercury flux measurements by micro-meteorological techniques. It was reported that daytime dry deposition velocities of GEM, PHg and RGM can reach 0.19, 2.1 and 7.6 cm s^{-1}, respectively while they are lower at nigh due to reduced atmospheric turbulence (Lin *et al.*, 2006).

In the modeling approach, the dry deposition rate of Hg^P is assumed to be equal to the dry deposition of fine PM, while for the case of Hg^{2+}, the deposition rate is assumed to be equal to that of HNO_3 or treated using resistance-modeling approaches. The advantages of using resistance model includes the accountant of effects of different land use as well as capture the diurnal variation of dry deposition velocities (Lin *et al.*, 2006). Equation of resistance model is express as the following:

$$V_d = \frac{1}{(r_a + r_b + r_c)} + V_g$$

Where

r_a: Aerodynamic resistance estimated from turbulent transport (s m^{-1})

r_b: Quasi-laminar resistance estimated from mercury diffusivities (s m^{-1})

r_c: Canopy/surface resistance (s m^{-1}). For mercury, r_c or canopy/surface resistance is the dominant term. The estimation of r_c is depends on the approaches of Wesley or Zhang (Environ International Corporation, 2011)

V_g : Settling velocity in case of particulate matter (Hg^P) (m s^{-1})

In the past, the modeling approach did not account for the deposition of Hg^0 as it is considered to be balanced with Hg natural sources. Recently, it was figured out that the account of natural emissions and dry deposition of Hg^0 enhances agreement between model output and observation (Lin *et al.*, 2010). The reason of that is although the dry deposition velocity of Hg^0 is much smaller compared to Hg^P and Hg^{2+}, its deposition may still be important due to the much greater concentration of Hg^0 compared to those of Hg^P and Hg^{2+}. Various values of dry deposition velocity of Hg species are summarized in Zhang et al (2009).

2.1.5.2. Wet Deposition

Among the Hg species, Hg^P is also assumed to be subject to wet deposition due to scavenging by cloud microphysics and precipitation, while Hg^{2+} is also expected to be scavenged readily by precipitation. Both Hg^{2+} and Hg^P have much lower Henry's law constants than Hg^0, and thus are assumed to partition strongly to the water phase. Wet deposition flux are estimated as function of precipitation intensity and total Hg^{2+} and Hg^P concentration in the aqueous phase. Uncertainties of wet deposition are in general due to uncertainties of precipitation. Wet deposition can be estimated using the following equations (Lin *et al.*, 2006)

$$F_{wet} = P \times \left[Hg^{2+}\right]_{aq,total}$$
$$F_{wet} = P \times (1 + K_a \left[APM\right]_{aq})\left[Hg_D^{2+}\right]_{aq}$$

Where

F_{wet} : Wet deposition flux (µg m^{-2} s^{-1})

P : Precipitation intensity of rain water (m s^{-1})

$\left[Hg^{2+}\right]_{aq,total}$: Total Hg^{2+} concentration in the aqueous phase (both dissolved and sorbed phases) can be expressed as $\left[Hg^{2+}\right]_{aq,total} = (1 + K_a \left[APM\right]_{aq})\left[Hg_D^{2+}\right]_{aq}$

K_a : Sorption constant

$\left[APM\right]_{aq}$: Aqueous concentration of atmospheric particulate matter

$\left[Hg_D^{2+}\right]_{aq}$: Dissolved Hg^{2+}

2.2. Air Quality Model Quantifying Atmospheric Hg Concentration and Deposition

Atmospheric Hg concentration and deposition in a specific area at a particular time can be obtained using a sampling or a monitoring method. However, sampling and monitoring of Hg are not always available for all the place and time of interests, in particular, in Southeast Asia region due to limitation of resources. Atmospheric modeling has been widely used to investigate atmospheric Hg concentration and deposition in which detailed information is discussed in Section 2.2.1.

Components for estimating Hg concentration using air quality models include meteorology, emissions, initial condition, boundary conditions, and choices of deposition schemes and photochemical driven.

2.2.1. Global Scale

There have been several works that investigated Hg fate using models on a global scale. Outputs of global model include global concentration and deposition maps which are useful to serve as initial condition and boundary condition for regional or local modeling assessment. Global 3D model of atmospheric mercury (GEOS-Chem) was used to interpret worldwide observations of total gaseous mercury (TGM) and reactive gaseous mercury (RGM) in terms of the constraints they provide on the chemical cycling and deposition of Hg.

It was either OH/O_3 driven (Selin *et al.*, 2007) or Br driven (Holmes *et al.*, 2010). In Selin et al (2007), present day versus pre-industrial cycles and anthropogenic enrichment factor for deposition was investigated. GEOS-Chem used assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-4). Emissions set were obtained from Global Emissions Inventory Agency year 2000 for anthropogenic Hg emissions. Hg emissions were added up 50% for Asian region and 30% for outside Asian region, which is suggested by another work on observations in Asian outflow (Strode *et al.*, 2008), to meet worldwide observation constrain. Hg^0 deposition was also included and proven as an important sink pathway. Hg^{2+} and Hg^P removal was by dry deposition with Wesley scheme and by wet deposition with a scheme including convective and large scale rainout and washout, as well as scavenging in wet convective updrafts.

2.2.2. Regional Scale

There were several studies on the investigation of Hg concentration and deposition in regional scale. In the following, summary of model's input and key assumption as well as model validation and finding is described.

In 1997, a Trace Elements Analysis Model (TEAM) was used to study the transport and fate of Hg emissions in the contiguous United States. The model has been tested with sulfur first to measure the uncertainties of meteorological input data and model parameterizations due to the similarity of sulfur and Hg (Pai *et al.*, 1997).

In a work published in 2002, Community Multi-scale Air Quality Modeling System (CMAQ) model coupled with MM5 was developed and modified to simulate atmospheric Hg and wet deposition. CMAQ had been adapted to simulate emissions, transport, transformation and deposition of atmospheric Hg in 3 species. Developments and modification include: Four new chemical reactions were added and cloud chemistry mechanism had been modified to include compound specific speciation for oxidized form of Hg, seven new aqueous phase Hg reaction, six aqueous Hg chemical equilibrium, two way mechanism for the sorption of dissolved oxidized Hg to elemental carbon. Partitioning of reactive gaseous Hg between air and cloud water was simulated based on the Henry's constant for Hg chloride. Henry's equilibrium was assumed for elemental Hg also. Particulate Hg was assumed to be incorporated into the aqueous medium during cloud nucleation. Wet and dry deposition was simulated for each of the three forms of Hg using assigned deposition velocity. Hg^0 deposition was considered equally to Hg^0 re-emissions from natural sources and does not account in this work (Bullock and Brehme, 2002).

In a work published in 2004, a Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) version 4 coupled with MM5 was developed and used to estimate the atmospheric fate and transport of Hg emissions in North America. The study provided estimates of the contribution of each source to atmospheric Hg deposition to the Great Lake. It was found that sources up to 2000 km from Great Lake contribute significant amount of Hg through atmospheric transport and deposition. Those sources were coal combustion as the largest contributor, followed by incineration and metallurgical sources.

Modeling atmospheric Hg chemistry and deposition for a 2002 annual simulation using MM5-CAMx has been performed (Yarwood *et al.*, 2003). The work, employing CAMx v4.5, also described model development, input database (including emission inventory, meteorology, and boundary conditions), and modeling results of sensitivity test and evaluation performance. An emissions inventory was obtained from the United States National Emissions Inventory. The simulation was performed for whole year period in total but was split into 2 computing periods (i.e., each simulation lasted 6 months). Boundary and initial conditions were obtained from CTM global models to the projection and vertical layers of CAMx. Dry deposition of Hg^0 was not investigated in this work.

In 2010, chemical transport of mercury in East Asia and the resulting mercury emission outflow were investigated for a number of emission inventory scenarios in an East Asian countires (Lin *et al.*, 2010). Emission inventory based existing national estimates (Streets *et al.*, 2005; Wu *et al.*, 2006) for year 2001. Emissions from outside China were from international estimates (Pacyna *et al.*, 2006) for year 2000. Emissions speciation followed literature review (Streets *et al.*, 2005). Emissions of Hg^0 from natural sources were prepared following the approaches of (Shetty *et al.*, 2008). Boundary and initial conditions were obtained from the outputs of a global 3-D chemical transport model, GEOS-Chem CTM (Selin *et al.*, 2007). Dry deposition of Hg^0 was also investigated in this paper. A study was performed four monthly simulations (January, April, July and October in 2005) using MM5-CMAQ-Hg version 4.6. Mercury emission outflow from the domain was estimated by calculating the chemical transport budget of mercury mass using CMAQ-Hg simulation results for each modeling month. Key findings of the work, described in the following quotes, include:

- “In the East Asian region for modeling year 2005, it was found that the annual dry deposition was 425 Mg, mainly contributed by Hg^{2+}, while the annual wet deposition was 396 Mg, mainly contributed by both Hg^{2+} and Hg^{P}. Anthropogenic emissions were responsible for up to 75% of the estimated deposition”
- “Regional mercury mass budgets showed strong seasonal variability, with a net removal of Hg^{2+} (7–15 Mg $month^{-1}$) and Hg^{P} (13–21 Mg $month^{-1}$) in the study domain, and a net export of Hg^{0} (60–130 Mg $month^{-1}$) from the domain for all four modeling months. The estimated annual emission outflow from the East Asian region was in the range of 1369–1671 Mg yr^{-1}, of which 50–60% was caused by emissions from natural sources. This represents about 75% of total mercury emissions (anthropogenic plus natural) in the region. About 65% of anthropogenic mercury emissions resulted in outflow, mainly into the Pacific.”

Annual simulations of atmospheric Hg in East Asia were performed using the Sulfur Transport and Deposition Model (STEM) coupled with RAMS to study Hg mass budgets in the region (Pan *et al.*, 2010). Regarding emission preparation for the simulation, Hg anthropogenic emissions were obtained from an existing database, which is from (Streets *et al.*, 2005) for 2009 emissions in China and (Pacyna *et al.*, 2006) for 2000 emissions outside China (e.g., Japan and Korea). Hg emissions from nature sources and re-emission were derived from the inventory in the year of 1999. Emissions from biomass burning (mostly in Hg^{0}) were estimated using global CO emissions and the Hg^{0}/CO ratio for biomass plumes observed during Ace Asia. Regarding to deposition treatment in the model, Hg^{0} dry deposition velocity was set to zero with assumption that its deposition flux can be balanced by the re-emission. This approach has been proven as reasonable assumption as it yields reasonable agreement between model simulation and observation (Bullock and Brehme, 2002; Cohen *et al.*, 2004). The dry deposition velocity for Hg^{2+} and Hg^{P} was calculated based on the parameterization of Wesley scheme for gaseous HNO_3 and sulfate deposition velocity, respectively. The wet removal of Hg^{2+} and Hg^{P} in STEM-Hg was treated similarly to that of nitric acid and sulfate aerosols, respectively. Key findings of the work, described in the following quotes, include:

- "Model-predicted annual mean concentrations of Hg^0, Hg^{2+} and Hg^P in the eastern and central China, Korea and Japan were 1.8 ng m^{-3}, 100 pg m^{-3}, and 150 pg m^{-3}, respectively. Ambient Hg^0 concentration exhibited seasonal variation with higher concentrations in winter and spring. Hg^P concentrations were higher in summer while Hg^2 concentrations did not show a clear trend."
- "Strong signals from large point sources strongly influenced the simulated mercury concentrations and depositions at both local and regional scales."
- "The estimated annual dry deposition and wet deposition in the domain were in the ranges of 590–735 Mg and 482–696 Mg, respectively. Mercury deposition was greater in the summer and the fall."
- "Boundary conditions had a strong influence on the simulated Hg concentration and deposition, contributing to 80% of the concentration and 70% of the deposition predicted by the model. The rest (i.e. 20% and 30%) was caused by the regional emissions before they were transported out of the model domain."
- "Using different oxidation rates reported for the Hg-O reaction led to a 9% difference in the predicted mean concentration and a 40% difference in the predicted mean deposition."
- "About 70% of mercury emissions ended up becoming mercury mass outflow, compared to the 75% reported by Lin et al. (2010) using CMAQ-Hg".

More recently, Hg seasonal depositions characteristics were compared to assess Hg pollution in the Yellow Sea using WRF-CMAQ, based on the 2007-2008 intensive measurement periods. The Yellow Sea is vulnerable to pollution, and the deposition of air pollutants could be used as a yardstick for estimating the long-range transport of air pollutants from China, which is located upwind of the western lies in the mid-latitudes. It was found that wet deposition was major removal pathway (about more than 90% of total deposition). Wet deposition was higher in July-2007 and January-2008 compared to October, 2007 and April, 2007, which was proportional with precipitation frequency and amount. About 97% of dry deposition was in the form of RGM, and, due to its high reactivity, its deposition occurred in the coastal areas near the emission sources than areas with high wind speed (Ghim *et al.*, 2011).

In Table 2.10 below, a list of existing models regarding Hg transport and deposition on regional and global scales is presented. Models used for the simulation of Hg atmospheric transport and dispersion vary in the formulation and scope of coverage depending on the investigated purpose.

Table 2.10: List of Model Applications to Study Hg Transport and Deposition (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)

Model	**Studied area**	**Resolution (km^2)**	**Gaseous reactant**						**Aqueous reactant**						**Dry Deposition**		
									Oxidation			**Reduction**					
			O_3	OH	H_2O_2	Cl	Br	HCl	O_3	OH	Cl^-	HO_2	SO_3^{2-}	*hv*	Hg^0	Hg^{2+}	Hg^P
GEOS-Chem	Global	4° x 5°	x	x	x	x	x		x	x		x		x	x	x	
GRAHM	Global	1° x 1°			x	x		x	x	x		x		x	x	x	
CTM	Global	8° x 10°	x	x	x	x	x	x	x	x	x	x		x	x	x	
ECHMERIT	Global	2.5° x 2.5°	x	x	x	x		x	x	x		x	x	x	x	x	
ADOM	Europe	55	x						x				x			x	x
CAMx	N.A	36 x 36	x	x	x	x			x	x	x	x	x	x	x	x	x
CMAQ	N. A. Asia	8 x 8 108 x 108	x	x	x	x			x	x	x	x	x	x	x	x	x
DEHM	N.H.	50 x 50 150 x 150	x						x				x			x	x
EMAP	Europe	50 x 50	x	x					x				x			x	x
HYSPLIT	N. A.	180 x 180	x	x	x	x			x	x	x		x			x	x
MSCE-HM	N.H. Europe	50 x 50	x	x		x			x	x	x		x		x	x	x
REMSAD	N. A.	36 x 36	x	x	x				x	x	x	x	x			x	x
TEAM	N. A.	100 x 100	x	x	x	x		x	x	x	x	x	x		x	x	x
STEM-Hg	East Asia	80 x 80	x	x	x	x			x	x	x	x	x	x		x	x
RAMS-Hg	N.A	36 x 36	x	x	x	x			x	x			x			x	x

N.H.: Northern Hemisphere

N.A: North America

2.3. Review on Data Preparation for Application of Air Quality Model to Investigate Hg Concentration and Deposition in Thailand

2.3.1. Emission Characteristics

Besides annual reported magnitude, emissions characteristics, such as temporal and spatial of emissions, are also important to present how emissions vary by time and space. Customarily, annual emissions were allocated into finer temporal resolution (i.e., month, day and hour) using temporal surrogates with a simple assumption that trends of emissions were proportional with those of surrogates.

Similarly, the spatial distribution of emissions was located as a point for large stationary sources/biomass burning or area (i.e., sub-district) for other small stationary sources. For area sources, in general, global and regional estimates often use population as surrogate with assumption that emissions are well spatial distribution with population. Then, all sources can be combined and allocated in gridded maps. Another important information to input in model is emitted height i.e., stack of power plant and large industrial facilities should be high from 50-200m while other areas sources are assumed to release emission near ground. For large combustion sources which classified as point, other stack parameters (i.e., stack diameter, exit velocity) which influence plume rise are also needed.

In addition, for the case of Hg where its speciation (Hg^0, Hg^{2+}, and Hg^P) has distinct physical and chemical characteristics, the exact fraction of each speciation is required to properly simulate the transformation of Hg in the atmosphere.

Besides Hg emissions, emissions of other Hg reactants are also needed. To investigate atmospheric Hg concentration and deposition, emissions of gaseous (i.e., NO_X, SO_2, CO, NMVOC, NH_3) and aerosols (PM_{10}, $PM_{2.5}$, OC, and BC) are needed. Up-to-date, regional emissions of such species have been developed and can be obtained. Examples of current database for Asia region are the REAS, INTEX-B and HTAP with details of sources included, spatial/temporal resolution are presented in Table 2.11 below.

Table 2.11: Available Dataset of Emissions Inventory Used as Gap-filling in This Work

Dataset	**Emission Sources**	**Species**	**Temporal Coverage**	**Spatial Distribution**	**Data Sources**
AMAP/UNEP	Global Anthropogenic	Hg^0, Hg^{2+}, Hg^P	2000, 2005, and 2010	0.5 deg	On request (Wilson, 2013)
INTEX-B (Zhang *et al.*, 2009)	Asia Anthropogenic	Group A[a]			http://cgrer.uiowa.edu/projects/emmison-data (Assessed by Nov 11, 2013)
SEAC4RS	Asia Anthropogenic	Group A[a]	2012	0.1 deg	http://www.cgrer.uiowa.edu/SEAC4RS/emission.html (Assessed by Aug 11, 2013)
REAS_v2	Asia Anthropogenic	Group A[a]	2008 (monthly) 2010 (monthly)	0.25 deg	http://www.nies.go.jp/REAS/ (Assessed by Nov 11, 2013)
HTAP-EDGAR	Global Anthropogenic	Group A[a], NH_3	2008 (monthly) 2010 (monthly)	0.1 deg	http://edgar.jrc.ec.europa.eu/htap_v2/index.php?SECURE=123 (Assessed by Nov 11, 2013)
GEIA	Global Natural	NO_X, SO_2, Cl_2	1990	1 deg	http://www.geiacenter.org/access/geia-originals (Assessed by Nov 11, 2013)
GFED.v3	Global Biomass Burning	Group A	1997– 2011	0.5 deg	http://globalfiredata.org/ (Assessed by Nov 11, 2013)

a) Group A: NO_X, SO_2, CO, NMVOC, NH_3, PM_{10}, $PM_{2.5}$, OC, BC

2.3.2. Meteorological Characteristics

Precise meteorological information is important for the dispersion model (Seaman, 2000). Generally, observations are normally too coarse in time and space (both vertical and horizontal) to serve as input for air quality models. In this case, meteorological models are recruited to generate details meteorological parameter in such details that required in air quality model. Outputs of meteorological model are need to validated with existing observation (e.g., temperature, wind speed and wind direction, relative humidity and precipitation) to ensure that it can capture key meteorological characteristic of interest in the studied domain.

Meteorological models were developed to serve for different scales of study from local to regional domains. There were a number of MM5 applications in Thailand. Some of them are for specific areas and specific purpose of interests, e.g., investigation for wind energy resources in Thailand (Manomaiphiboon, 2009; Phan and Manomaiphiboon, 2012). Another investigation on physical option to simulate precipitation in Thailand among 2 set of physical options (i.e., Kuo and Grell schemes in Songkha and Hatyai provinces) was performed. It was found that Kuo schemce show the precipitation in a case of accumulated convective precipitation and Grell scheme show the precipitation in a case of accumulated convective precipitation. It was concluded that these 2 schemes could be used to forecast the precipitation in Thailand. However, the different between observation and simulation was still in factor of 2 (Sirikantisopon, 2001).

More recently, MM5 has been applied for investigate meteorological parameter in assisting effort in solving ozone issues in an industrial area-Map Ta Phut Industrial Estate-Rayong Province, Thailand (Industrial Eastate Authority of Thailand-IEAT, 2004) with the suggestion of US EPA that the physical option which use for Texas case may fit well for the case of urban areas of Thailand (Environmental officer at Pollution Control Department, 2012). Besides that, a number of air quality oriented studies which used MM5 can be listed such as the work of investigation of impact of atmospheric biomass emissions to air quality in Thailand and Southeast Asian region using STEM2K1 (Thongboonchoo, 2005) or investigation of ozone impact in Thailand using CMAQ (Le, 2008).

2.3.3. Observation Data for Model Verification

There was a long term monitoring network for mercury deposition, called Mercury Deposition Network (MDN). It has been quoted that “The MDN is the only network providing a long term record of total mercury (Hg) concentration and deposition in precipitation in the United States and Canada. All MDN sites follow standard procedures and have uniform precipitation chemistry collectors and gages. The automated collector has the same basic design as the NTN collector but is modified to preserve mercury. Modifications include a glass funnel, connecting tube, bottle for collecting samples, and an insulated enclosure to house this sampling train. The funnel and connecting tube reduce sample exposure to the open atmosphere and limit loss of dissolved mercury. As an additional sample preservation measure, the collection bottle is charged with 20 ml of a one percent hydrochloric acid solution” (National Atmospheric Deposition Program, 2012).

In Thailand, atmospheric concentration and deposition has not been available. In year 2010, during the Dongsha Campaign to investigate the distribution of atmospheric Hg in northern Southeast Asia and southern China, samplings of Hg concentrations were conducted at 2 sites: Da Nang City, Vietnam and Chiangmai Province, Thailand. In Thailand, the only total Hg atmospheric concentration measured in year 2010 in the northern of Thailand shows daily average values of 2.03 ± 0.15 ng/m3 during 24th – 31st March, 2010 and 2.34 ± 0.44 ng/m^3 during 10th – 18th April, 2010 (Sheu et al., 2013).

In Thailand, Hg concentrations in water (i.e. river, coastal water, industrial estates, offshore), sediments (i.e. coastal sediments, industrial estates, offshore), and aquatic tissues in river mouths, coastal areas, industrial estates, and offshore and living tissues are biannually investigated. In most cases, Hg concentrations are less than the Thai standards except at some points near industrial waste discharges (Pollution Control Department, 2001).

A local study on the distribution of Hg in surface soils and rice grains in the area within the 30-km-radius of the lignite coal-fired power plant in Lampang Province, Thailand was investigated. Samples of soils and rice grains were collected to estimate the environmental potential risks by Hazard Quotient Equation (HQ). The results revealed that the distribution of Hg both in surface soils and rice grains occurred in all areas around the power plant with low risk threat (HQ <1) (Meemuk, 2011).

2.4. Chapter Summary

While Hg emission inventories in Thailand exist, they are still insufficient in terms of details that can be served to air quality modeling. This work aims to update Hg emissions. To estimate Hg emissions in Thailand where some source-specific information was available but not comprehensive, a mixture between these two approaches, which toward to bottom up approach for the case of this study in which both statistical (i.e., top-down) and source-specific (bottom-up) information were combined. In particular, activity data were obtained from local organization through technical reports or survey whereas EFs were adopted from literatures for the case of Thailand. Spatial, temporal and speciation characteristics of emissions were investigated. Details of development are described in Chapter 3.

Meteorological models are an important pathway to assess the transportation of the air mass. The MM5 model was chosen to prepare meteorological input for air quality model. Though MM5 has been widely applied in Thailand, there was no application for the whole country for different seasons, which can be used to access the seasonal variation of Hg concentration and deposition. Simulations on different combination set of physical parameters are run to investigate to present best approach. Details information is presented in Chapter 4.

Modeling applications to investigate Hg concentration and deposition in Thailand has not been available. To do so, regional model such as CAMx or CMAQ was firstly considered. Among that, CAMx was chosen due to its capacity to cover most up to date Hg chemical reactions (Environ International Corporation, 2011). In additional, flexible input/output procedures and supported tools are useful for the case of Thailand, where details of EI development are not originally fitted well with CMAQ’s emissions models (i.e. SMOKE). Detailed information is presented in Chapter 5.

CHAPTER 3
EMISSIONS INVENTORY

This chapter presents the theories, methods and materials of estimating atmospheric Hg emissions in Thailand in details. Results and discussion on magnitude as well as emissions characteristic are included. This chapter is, therefore, expected to fulfill objective 1 of this thesis, i.e., "To investigate and to assess Hg emissions sources in Thailand". To serve as input to air quality model, characteristics of emissions including emissions in a specific time (i.e., hourly) and specific place (i.e., grid) are needed. First of all, annual emission is estimated by recruiting bottom up and top down approaches as well as the integrated approach, a so called semi-bottom up, then temporal, spatial and speciation surrogates are used to characterize emissions to meet first objective and process the annual emissions to model ready input.

3.1. Materials and Methods

3.1.1. Source Classification

- Natural sources include in-land watershed and soil surfaces. Emissions from sea surfaces were not included in these estimates; however, they are available and can be obtained from the literature (Ttravnikov, 2013).
- Anthropogenic sources include combustion sources (i.e. thermal power plant, industrial facilities, and incinerators) and industrial processes (mineral production, metal production).
- Biomass burning includes agricultural residue burning and forest fires.

3.1.2. Emission Estimation Method

Customarily, the magnitude of emissions of species is a function of the emitted process which defined by the emissions factor, the intensity of the processes surrogated by activity data. The activity data in this work are mostly from country specific sources while emissions factors were adopted from foreign sources, therefore, uncertainties of this estimates are mostly from the uncertainties of emissions factor.

3.1.2.1. Natural Sources

Emissions from water and soil surfaces can be estimated using the following equation:

$$E = S \text{ x } T \text{ x } EF$$

where

E = Emissions (kg)

S = Water/soil surface area (km^2)

T = Released duration (hr). As Thailand is located in a tropical area, its released duration of natural Hg due to surface evaporation was assumed to be during the daytime and the whole year long (i.e., 365 days).

EF = Released flux ($kg\ km^{-2}\ hr^{-1}$)

3.1.2.2. Anthropogenic Sources

Emissions from internal combustion were estimated using the following equation:

$$E = EF_{uncontrolled} \times (1-ER/100) \times A$$

or

$$E = EF_{controlled} \times A$$

Where

E = Emissions (kg)

A = Fuel consumption rate (GJ) of a source

EF = Emission factor ($kg_{\text{Hg emitted}}$/GJ) is a function of Hg content fuel

ER = Emissions reduction (in percent)

Emissions from industrial processes were estimated using the following equation

$$E = EF_{uncontrolled} \times (1-ER/100) \times A$$

or

$$E = EF_{controlled} \times A$$

Where

E = Emissions (kg)

A = Production (ton) of a source

EF = Emission factor ($kg_{Hg\ emitted}$/ton)

ER = Emissions reduction (in percent)

3.1.2.3. Biomass Open Burning Sources

Emissions from biomass burning were estimated using the following equation:

$$E = A \times B \times C \times EF$$

Where

E = Emissions (kg)

A = Area burned of biomass (m^2)

B = Biomass loading ($kg_{dry\ mass\ biomass}/m^2$)

C = Combustion efficiency

EF = Emissions factor ($kg_{Hg\ emitted}/kg_{dry\ mass\ biomass}$)

3.2. Activity Data

As stated above, the study aims to utilize published data from available governmental/non-governmental projects or academic research. Table 3.1 below summarizes of Hg emission sources, activities data and their sources used to estimate emissions, and the sources of information to compile emissions for inventory year 2010. The Table 3.1 presents in details activity data. To obtain better information from lacked-reported- industrial sources, Environmental Impact Assessment (EIA) reports are used. However, the EIA reports are just available for large industrial facilities only. For other certain types of sources for which there is lack of information, other methods where resources are available have also been additionally implemented such as phone surveys, site visiting surveys and expert judgments.

Table 3.1: Activity Data Used in This Work

Hg emission sources		Activity Data	Source of Data
Natural		Area of soil surface and water surface	LDD
Anthropogenic	Combustion in Power plants	Amount of fuel combusted	EGAT, DEDE, EPPO
	Combustion in Industrial facilities	Amount of fuel combusted	DIW, DEDE
	Combustion in Waste incinerator	Amount of waste incinerated	NSO
	Non-combustion in Industrial processes	Amount of industrial products generated	OIE, USGS, DPIM
Biomass open burning		Area burned, land use map	MODIS, LDD

<u>List of organizations and corresponding data sources:</u>

DEDE	Department of Alternative Energy Development and Efficiency, Thailand
DIW	Department of Industrial Works, Thailand
DPIM	Department of Primary Industrial and Mines, Thailand
EGAT	Electricity Generating Authority of Thailand
EPPO	Energy Policy and Planning Office, Thailand
LDD	Land Development Department, Thailand
MODIS	Moderate Resolution Imaging Spectroradiomete
NSO	National Statistic Organization, Thailand
OIE	Office of Industrial Works, Thailand
PCD	Pollution Control Department, Thailand
USGS	United States Geological Survey

3.2.1. Natural Sources

Atmospheric Hg emissions are naturally emitted from soil and water surfaces. To estimate atmospheric emissions from this source, activity data is areas of surfaces (i.e. area of soil and water). The information was obtained from the Land Development Department - LDD (Land Development Department - Thailand, 2010). The department collects information of land cover data for the whole country. The latest released version is year 2007. In Thailand, land area can be grouped to forest land, agriculture land, urban and built-up land, water body and other miscellaneous land. In Table 3.2 below, percentage share of land areas in Thailand in year 2007 are estimated based on land use map year 2007. As seen, agricultural land and forest land have largest share, which account for 52.66% and 36.64% of total areas, respectively. Most of forest areas located in the Nothern regions of Thailand while agricultural land was domiant in the Northeastern, Central and Southern regions.

Table 3.2: Land Area of Each Category Following LDD Classification In 2007 (Land Development Department - Thailand, 2010)

Symbol	Land Classification	Areas (km^2)	Percentage
F	Forest Land	187,996	36.64
A	Agricultural Land	270,205	52.66
U	Urban and Built-up Land	23,728	4.62
W	In-land Water Body	12,694	2.47
M	Miscellaneous Land	18,489	3.60
Total		513,114	100.00

3.2.2. Anthropogenic Sources

3.2.2.1. Stationary Combustion

Hg emissions of this category were emitted due to the impurity of fuel combusted and combustion type. This section includes fuel combustion for energy, steam, heat generation and waste disposal processes. For combusted sources, Hg content in fuels is a main factor that influences emissions. Hg content is generally high in low-level coal, followed by bio-fuel and oil. Coal used in Thailand is produced in Thailand or imported from nearby countries (i.e.

Indonesia and Vietnam) and Hg containing in fuel of various countries, resulting from measurements are available from literature (United Nation Environment Programme, 2011). Combustion technology (i.e. boiler configuration and air pollution control devices) affect Hg transformation in the boiler and thus influences Hg speciation and Hg reduction.

a) Activity Data Collection for Estimating Hg Emissions from Fuel Combustion for Thermal Power Plants

To estimate emissions from fuel combustion for thermal power plants in Thailand, activity data (e.g. fuel composition, fuel consumption, boiler configuration, and emissions control devices) were obtained from 3 main power producers, i.e. Electricity Generating Authority of Thailand (EGAT), Independent Power Producers (IPP), and Small Power Producers (SPP). Thermal power plants in Thailand use locally mined lignite, imported bituminous and anthracite as well as other fuel such as biomass as fuel from residue agriculture waste. Plants' information were available for each EGAT and IPP plant (Department of Alternative Energy Development and Efficiency, 2011) whereas they are only assessable by sector for each SPP (Energy Policy and Planning Office, cited 2011). Information of fuel consumption from power plants were annually collected and published by the Department of Alternative Energy Development and Efficiency (DEDE) (shown in Table 3.3).

Table 3.3: Fuel Consumption in Power Plants in Year 2010 (Department of Alternative Energy Development and Efficiency, 2011)

Sector	**Fuel Oil (liter)**	**Diesel Oil (litre)**	**Lignite & Coal (ton)**	**Natural Gas (MMscf)**	**Biomass (ton)**			
					Paddy Husk	**Bagasse**	**Agricultural Waste**	**Municipal Waste**
EGAT	140,084,467	12,431,995	16,004,196[a]	430,519	-	-	-	-
IPP	95,234,067	14,116,208	3,672,987[b]	492,033	-	-	-	-
SPP	5,156,956	102,423	736,816[c]	96,878	771,043	2,434,434	1,169,555	-
VSPP	-	12,461,171	24,009	4,458	528,417	2,053,774	186,805	29,193
TOTAL	240,475,490	39,111,797	20,438,009	1,023,888	1,299,460	4,488,208	1,356,360	29,193

a) Lignite

b) Sub-bituminous coal

c) Anthracite

In Thailand, most power plants are located in the Central and Eastern regions. There are 2 large coal-fired power plants. One is EGAT power plant, located in the Northern region of Thailand. Another one is IPP power plant, located in the Eastern region of Thailand. Several coal-fired plants under SPP and VSPP are located in the Central and Eastern regions of Thailand.

b) Activity Data Collection for Estimating Hg Emissions from Fuel Combustion for Industrial Facilities

In Thailand, industrial economics has been playing an important growth in national development. After the recovery of the economic crisis, fuel consumption for industrial activities has been increased 17% - 21% per year (Department of Alternative Energy Development and Efficiency, 2011). Industrial facilities are classified into 107 types, which can be further grouped to 9 main types (i.e., Food and Beverage, Textile, Wood and Furniture, Paper, Chemical, Non-Metal, Basic Metal, Fabrication, Other-Unclassified). Fuel consumption of different fuel type (coal & lignite, diesel oil, fuel oil, fuel wood, bagasse, paddy husk etc.) of each (of 9 types above) was obtained from governmental reports (Department of Alternative Energy Development and Efficiency, 2011). Information on factory’s registration, installed capacity, budget investment as well as address was available from the DIW database. Fuel consumption data for each industrial facility, important to estimate emissions, was not available. Instead, fuel consumption data is available for each economic sector; therefore, the derived emissions factor (kg/kWh) was calculated based on the share of the fuel consumption of each sector obtained from the EPPO. For some factories, location of latitude and longitude is also provided by the factory also and available upon requested from the DIW. Large industrial facilities were equipped with Air Pollution Control Devices (APCDs) which details were collected from Environment Impact Assessment (EIA) reports (Office of Natural Resources and Environmental Policy and Planning, 2012). In Thailand, large numbers of industrial facilities are commonly located in the Central and Eastern regions (DIW, 2012).

Table 3.4: Fuel Consumption in Industrial Facilities in Year 2010 (Department of Alternative Energy Development and Efficiency, 2011)

Sector		**Food and beverages**	**Textiles**	**Wood and furniture**	**Paper**	**Chemical**	**Non-metallic**	**Basic metal**	**Fabricated metal**	**Others**
Coal & its products	Bituminous	-	169	-	3,380	380	20,826	-	-	-
	Anthracite	-	-	-	-	-	3,126	4,562	-	-
	Coke	-	-	-	-	-		7,477	-	-
	Lignite	254	127	-	1,225	254	35,654		-	-
	Other coal	-	-	-	465	66,957	163,358	3,971	-	35,907
Petroleum product	LPG	1,648	1,014	85	338	9,885	5,238	5,281	5,196	9,251
	ULG 91	0[a]	42	42	0[a]	85	0[a]	0[a]	42	211
	ULG 95	0[a]	0[a]	0[a]	42	0[a]	42	-	42	42
	Kerosene	42	422	0[a]	0[a]	127	42	42	85	0[a]
	HSD	12,335	634	1,436	1,183	3,253	2,154	1,394	1,690	9,970
	LSD	-	-	-	-	-	-	-	-	-
	Fuel oil	8,871	2,281	85	1,859	3,380	1,098	5,999	718	12,800
Natural		4,393	1,141	0[a]	0[a]	34,344	32,105	10,434	3,211	6,083
Renewable energy	Fuel wood	12,842	-	549	-	3,760	5,703	-	-	-
	Agricultural waste	67,252	-	1,352	0[a]	9,420	36,330	-	-	-
	Paddy husk	41,272	-	-	0[a]	-	760	-	-	-
	Bagasse	114,270	-	-	-	-	-	-	-	-
Total		305,086	33,500	9,758	16,306	170,539	328,954	63,493	63,493	77,264

a) Less than 0.05

c) Activity Data Collection for Estimating Hg Emissions in Incinerators

In Thailand, there are 3 common ways to treat waste, i.e. landfills, incineration and recycling. In addition, in some rural areas where is lack of waste management system, unsecured landfills or open dump burning are still illegally existed. While landfills cause more or less contamination on soil and water, waste incinerators are source for atmospheric pollution (United Nation Environment Programme, 2011) which atmospheric Hg emissions are emitted during combustion of Hg containing wastes such as thermometer, fluorescent lamp etc. According to governmental report (Pollution Control Department, 2012), waste to incinerator includes municipal solid, medical, and industrial hazardous wastes. Another incineration source is crematory, which is considered as air polluted source in Thailand where according to statistic, up to 95% of population is with Buddhism religion belief. In Thailand, for incinerator to burn municipal waste, only one large incinerator was operated in year 2010. The incinerator has capacity of 250 ton/day located in Phuket province, Southern of Thailand. For industrial hazardous waste, there are 2 kinds of incinerators. The first type is especially for industrial hazardous waste, the second type is boiler in cement factory, which purchase industrial waste and use as fuel. In year 2010, there is 5 cement plants (of total 14 cement plant) burning hazardous waste. Sources of data is PCD Annual reports (Pollution Control Department, 2012)

Table 3.5: Amount of Waste to Incinerator in Year 2010 (Pollution Control Department, 2012)

Source	Activity Data (ton)
Municipal waste (MSW)	92,659
Medical (infected) waste	40,785
Hazardous industrial waste	987,528
Crematories	373,399 (body)

3.2.2.2. Industrial Processes

Besides Hg emissions through combustion processes, some industrial facilities emit atmospheric Hg through non-combustion processes due to (1) the intentional use of Hg substances as catalysts or input materials, such as caustic soda (Hg leaks), batteries or (2) Hg impurities in raw materials during production processes of cement, pulp and paper, and (3) Hg leaked during material extraction from the Earth's crust.

To identify key industrial Hg emissions sources in Thailand, the authors have reviewed the literature (US-EPA, 1997; United Nation Environment Programme, 2011), consulted with local experts (personal communication environmental officers from the Pollution Control Department-PCD, Department of Industrial Primaries and Mines-DIPM, Office of National Resources and Environmental Policy and Planning-ONEP) of potential industrial sources in Thailand to figure out whether or not Hg emissions are currently released in the processes in the year 2010-the time of the emissions estimation. Only following industries were accounted due to the continuing potential of Hg emitter in Thailand: metal (e.g., Au, Fe, steel, and Zn) production (by sintering and blast furnace steps), cement production (dry process-kiln and preheating/precalcining steps), pulp and paper production (Kraft process-pulping process). Other industries were not included because by the year 2010, either they have not been existed (e.g., Hg primary production or pig iron production) or no Hg was used in their processes (e.g., caustic soda). Emissions from industrial processes were discussed in details in sections following.

a) Activity Data Collection for Estimating Hg Emissions from Non-Combustion Processes in Cement Plants

According to the cement association of Thailand Information of the scale of the cement industry 2012 presented that there are 8 companies with 14 plants (total 31 kilns). Production capacity are reported as 49,916 thousand ton clinker or 56,422 thousand ton of cement. Actual cement production in year 2012 are 33,757 thousand ton with domestic sales are 27,989 thousand ton) (Thailand Cement Manufacturers Association, 2013). In year 2010, cement production is 36,496 thousand ton. Material included limestone, shale, marl and gypsum. Most of cement factories located in Saraburi province, Thailand which is near mining source of limestone (locations of cement plants are available in Thai Cement Manufacturing Association webpage http://www.thaicma.or.th/cms/index.php/location-of-cement-plants/).

There are also 5 factories that also received industrial hazardous waste to mix as material. The fuels are used in cement factory are mostly lignite and coal from Meamoh mining which is transported to manufacturing sites by train. The product after burnt is clinker, which is grinded and mix with gypsum to produce cement. Gypsum are collected from imported gypsum, bottom ash from coal fired boiler as well as own mining. This cement is mixed again with fly ash to produce different level and quality of cement to meet with different construction demand (for example, mixture of much fly ash will produce weak cement for wall construction while more cement will produce more strength-intensive-material).

b) Activity Data Collection for Estimating Hg Emissions from Non-Combustion Processes in Pulp and Paper Plants

Paper production in Thailand is from both new produced pulp and recycled material. The production of new material is from 5-7 years old eucalyptus trees, which are mostly planted in the Northeastern of Thailand. This small wooden piece is boiled together with chemical liquid (i.e., (sodium hydroxide and sodium sulfide used to separate lignin from the cellulose fibers needed for papermaking) during pulping process and produce black liquor as by product. Black liquor is defined as “black liquor is the spent cooking liquor from the Kraft process when digesting pulpwood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers”. To produce a ton of pulp, it produces up to 7 ton of black liquor. With the invention of recovery boiler in year 1930s, up to 95-99% of black liquors is reused as fuel and recover chemical liquid for next use. Black liquor also contains some sources of energy can be used as fuel in combustion (Biermann, 1993). Some pulp and paper plants also generate steam and electricity, in which Hg emissions were mainly released during chemical recovery furnaces of black liquor. Therefore, to estimate Hg emissions from pulp and paper industry, either the amount of primary pulp and paper production or the amount of black liquor consumed was used. Hg content in black liquor is 0.02 g/ton (United Nation Environment Programme, 2011). To avoid double counting as emissions from black liquor combustion has been estimated in combustion section, this was not estimated here again.

c) Activity Data Collection for Estimating Hg Emissions from Non-Combustion Processes in Iron and Steel Plants

There is no primary iron and steel production in Thailand. In 2010, 967,937 tons of iron ore was mined in Thailand (http://www.ptkmining.com/aboutus.asp). However, all of them are exported for further processes. Hg emissions are mostly emitted through process of sintering and blast furnace which assessed by the amount of pig-iron produced. There was no production of pig iron in Thailand in year 2010; therefore, Hg emissions from iron and steel production in Thailand were neglectable. Some amount of iron and steel was recycled in year 2010 but there did not contribute as a signification source of Hg emissions.

d) Activity Data Collection for Estimating Hg Emissions from Non-Combustion Processes in Non-Ferrous Metal Plants: Large scale gold mining and production

In 2010, gold production in Thailand was 4,045,568 grams of ore (DPIM, 2012). A company, named Tungkum Limited located in Loei province, Northeast region in Thailand was licensed to mine and extract gold in Thailand. Since year 2006, company’s capacity of ore processing is 1,200 to 1,500 ton per day, depending on ore qualities. The Company expects to process about 440,000 tons of ore per annum. Technique use is a so called “Carbon in leach” (http://www.tongkahharbour.com/Tongkah/company_TKL.html). The processes are described by the following quote: “The ore extraction process is essentially the carbon-in-leach (CIP) method in combination with closed-circuit processing technology (recycling with no release of solutions used in ore treatment into down-stream areas). Ore is fed to a primary crusher then conveyed to the ball and mills for finer grinding. The product is then pumped through a chemical processing sequence by which the gold is taken into solution by leaching and cyanidation and, subsequently, extracted and adsorbed onto activated carbon, and the surplus cyanide solution is recycled back into the process. The gold-loaded carbon is then treated to extract the gold from the carbon using the established electro-winning process. The impure gold is then melted and poured to form gold bars (dore), and the solution is recycled. The dore bars are then sent to an external refinery to be refined to 99.99 % purity.”

e) Activity Data Collection for Estimating Hg Emissions from Non-Combustion Processes in Non-Ferrous Metal Plants: Zinc Mining and Production

In Thailand, ore Zinc mine is located in Tak Province, Northern region under Padang Industrial Limited (http://www.padaeng.com). Three are operating sites - Mae Sod mine, Tak smelter and Rayong roaster. In Thailand in year 2010, Zinc ore which are mined in Thailand are Zinc Silicate (amount of ore is 146,470 ton) and Zinc ore which are imported are Zinc sulfite (amount of ore is 174,586 ton). In year 2010, Zinc production in Thailand is 55,529 ton (DPIM, 2012).

Normally, the Zinc content in Zinc ore is 5-15%, and it is needed to be concentrated at 55% before being used by a smelter. At first, sulfur in the concentrate are removed by roasting or sintering process by heating the concentrate to the temperature of 900^{o}C, Zinc blende (ZnS) will be convert to ZnO and SO_2 and subsequently convert to H_2SO_4. In the second phase, hydrometallurgical process (or electrolysis process) are used to extract ZnO from other calcines. It consists of 4 steps: leaching, purification, electrolysis, melting and casting. In the leaching process, ZnO have reacted with SO_3 to form $ZnSO_4$ (liquid or leaching product) while Lead and Silver is retained as solid part. In leaching products, other metal such as Copper, Cadmium, Arsenic are still remained, and thus need to be purified. In the purification process, Zinc dust and steam are used to remove copper, cadmium, cobalt, nickel etc. After purification, the concentration of impurities should be lesser than 0.05µg/l. At this stage, the Zinc sulfate solution can be input for electrowinning. In electrolysis step, Zinc is extracted from purified Zinc sulfate solution by electrowinning. In melting and casting process, Zinc ingots or alloyed ingots are produced.

Table 3.6: Industrial Production from Key Mercury Industrial Sources in Year 2010 (Department of Primary Industries and Mines, 2011)

Emissions Sources	Amount (ton)
Gold (large scale)	4.1
Zinc	55,529
Cement	36,496,000

3.2.2.3. Manufacturing/Use/Disposal of Hg-Containing Products

Hg-containing products are banned and it is assumed that there is no production in Thailand (Pollution Control Department, 2001). Most of these products have been imported. For example, more than 90% of clinical thermometer are import from China and batteries as well as fluorescent lamp are from Japan and China (The Custom of Thailand, 2012).

The concerns of Hg in these sections are from the use and disposal treatment of these products. Major parts of Hg-containing products were treated as hazardous wastes in secure landfills or hazardous incinerators. Incinerators are also included in the incinerator sections under municipal waste and medical waste.

3.2.3. Biomass Open Burning

Biomass burning, especially forest fires and agricultural residue burnings, is an on-going man-made activity in Thailand. Therefore, it can be accounted as either reemission source or anthropogenic source. The amount of biomass burnt can be estimated using questionnaire surveys as well as from satellite image. Information of 0.5 deg resolution of hotspots in year 2010 derived from satellite is available from GFEDv3 (Randerson *et al.*, 2006) and that of 1 km resolution is available from FIRMS (National Aeronautics and Space Administration, cited 2012).

To estimate Hg emissions from biomass burning in the case of Thailand, 1 km resolution hotspots (i.e. locations of fire) captured by MODIS were obtained from the FIRM database (National Aeronautics and Space Administration, cited 2012). The values available in monthly basis indicated that January to April is biomass intensive burning period, not only by Thailand but also other countries in Greater Mekong Sub region (Bonnet and Garivait, 2011). The location of hotspot then was overlaid with land use map from the LDD to identify land cover over the hotspot. This information is useful to allocate precise land cover-depended factor such as biomass loading and combustion efficiency. Fuel density of each land use type, obtained from local survey and measurement. For forest fire estimation in Thailand, Junpen and coauthors estimated that biomass density is 371.4 ton dry mass/km^2 for deciduous dipterocarp forest and 364.5 ton of dry mass/km^2 for mixed decidous forest and combustion completeness is 0.78 for both deciduous dipterocarp and mixed decidous forests (Junpen et al., 2011). For agricultural burning, biomass density is 237 ton/km^2, 620 ton/km^2, and 247 ton/km^2 and combustion completeness is 0.87, 0.2 and 0.39 for rice, corn, and sugar cane, respectively (PCD, 2007; Cheewaphongphan *et al.*, 2011).

Table 3.7: Burnt Areas Detected by MODIS in Thailand in Year 2010

Land Use Type		Area Burnt[a] (km^2)	Combustion Completeness (ratio)	Biomass Density (ton of dry mass / km^2)
Agriculture	Total	2,208		
	Paddy field	1,215	0.87[b]	237[b]
	Corn (or Maize)	670	0.2[c]	620[c]
	Sugarcane	323	0.39[c]	247[c]
Forest	Total	7,228		
	Mixed Deciduous	2,971	0.78[d]	365[d]
	Deciduous Dipterocarp	1,552	0.78[d]	371[d]
	Other types of forest	2,705	0.78[b]	368[e]

a) FIRM Database (National Aeronautics and Space Administration, cited 2012), confidential level is 75%

b) (Cheewaphongphan et al., 2011)

c) (PCD, 2007)

d) (Junpen et al., 2011)

e) Average values of mixed deciduous and deciduous dipterocarp

3.2.4. Notes on Quality Assurance and Quality Control (QA/QC) for Activity Data Collection

Activity data was collected from governmental organizations with assuming that they have passed QA/QC. Data was compared whenever it is available. For activity rate, since most of the data were secondary data obtained from governmental and private organizations, it is reasonable to firstly assume that the data have been passed through QC processes of these organizations. Nevertheless, the activity data has been rechecked by comparisons among different organizations, if available. The expert's evaluation has been accounted in making any assumption. In additional, for any steps related with calculation, "double-check" concept was applied.

3.2.5. Spatial Distribution of Hg Emissions Sources

Emissions inventory is often presented as a single value for a whole country or a sub-region of interest due to the availability of activity data. If the estimation approach is top down, emissions of a large domain is estimated first and then allocated to finer administrative region using proper surrogate. This approach is often recruited in global or regional estimation (Pacyna et al., 2003; Pacyna et al., 2010). If estimation approach was bottom up, source location was already known and allocated directly to the map. Spatial distribution of emission provides more accuracy details on spatial distribution of emissions. However, this step provides spatial allocation in irregular shape. To provide as input to modeling, emissions are need to be in grid format, in line with grid size and projection in the meteorological model. In section below, surrogate to allocate emissions to finer resolution is described.

Besides magnitude, information on the locations of sources is very important in presenting the originality of the sources. The more details information of source is, the higher accuracy in modeling assessment is. Exact coordinate (latitude/longitude) as well as geographical terrain height of each single source are desired. However, this information is just available for large facilities such as large power plants and large industrial plants. In this case, this source was put in the Geographic Information System map as point. For area sources, due to large number of sources which cannot obtain information, emissions are grouped as use suitable surrogates to spatially allocate. Each source has been allocated to the finer possible resolution and then spatially allocated to modeling grid of interested solution. In Table 3.12 below, surrogates are used to spatially allocate atmospheric Hg emissions.

Table 3.8: Surrogates Used to Spatially Allocate Hg Emissions

Emission Sources		**Surrogates**	**Sources of Data**
Natural Sources		Land use	(Land Development Department - Thailand, 2010)
Anthropogenic Sources	Power plants	Lat/Lon	(ERC, 2012)
	Industrial facilities	Lat/Lon	(DIW, 2012)
	Waste incinerator[a]	Sub-district	(DIW, 2012)
	Other[b]	Provincial Population	(Pollution Control Department, 2012)
Biomass Burning		Hotspot location	(National Aeronautics and Space Administration, cited 2012)

a) Municipal waste incinerator and hazardous waste incinerator

b) Medical waste incinerator

3.2.5.1. Natural Sources

For natural sources, emissions are a function of surface areas (i.e., soil and water). A surface area map was obtained from the LDD for the latest year released in 2007. Then surface map can be further allocated to grid size of interests.

3.2.5.2. Anthropogenic Sources

Spatial distribution techniques of stationary sources differed, depending on detailed level of data obtained. If all information of sources location was available in latitude and longitude, action of allocating emissions from those sources to map is straight forward. For the case of Thailand, most of power plants belonged to the EGAT and IPP are considered large and information of latitude and longitude was available. For SPP power plants, only name of sub-district was available. Maps of administrative boundary (province, district and sub-district) of Thailand was obtained from the ESRI maps and locations of SPP power plants were assumed as center latitude and longitude of sub-district that they were located. There was a name of a sub-district that did not match with the database. In this case, the website of the yellow pages **(**www.yellowpages.co.th/en/*)* was used to search for the up to date address (or at least name of sub-district) following the name of the power plants before located to ESRI maps again. Industrial facility's sub-district name was obtained from the DIW database. Similar assumption and approach (as applied for SPP power plants) was used to allocate emissions from industry to sub-district's center coordinate.

3.2.5.3. Biomass Burning

Re-emission sources here means biomass burning. Information was available in latitude and longitude for hotspot with resolution is 1 km. Therefore it is reasonable to assume that resolution of biomass burning is 1 km. Emissions from this source was directly allocated to grid cell.

3.3. Emission Factors

In this work, emission factors were obtained from published EFs literature review (without any own measurement). In the section below, details of EFs were reviewed and the chosen was presented.

3.3.1. Natural Source

Emissions factors to estimate Hg emissions from soil and water surfaces were obtained from the literature review due to lack of local measurements on emissions flux. Some of measurements are described below.

Emissions factors from natural sources in an industrial province, Chongqing Province, China, were estimated using dynamic flux chamber technique from selected natural sources (i.e. several water bodies and soil sites from both contaminated and uncontaminated (Wang *et al.*, 2006). There are 6 soil sites in three different areas (mercury polluted area, farmland and woodland) and 4 surfaces of in land water bodies from August 2003 to July 2004. Emissions rates were 3.5 ± 1.2 $ng.m^{-2}h^{-1}$ to 8.4 ± 2.5 $ng.m^{-2}h^{-1}$ for shaded forest sites, 85.8 ± 32.4 $ng.m^{-2}h^{-1}$ for farming field site, 12.3 ± 9.8 $ng.m^{-2}h^{-1}$ to 733.8 ± 255 $ng.m^{-2}h^{-1}$ for grassland and manmade forest site and 5.9 ± 12.6 $ng.m^{-2}h^{-1}$ to 618.6 ± 339 $ng.m^{-2}h^{-1}$ for water bodies. It was figured that the release flux of mercury from air-water surface were generally higher than that for air-soil surface and negative flux for both sources were observed at night on an overcast day and during winter. To estimate natural emissions in the domain, mean value of released flux in the end of summer was selected to represent the release flux of the whole year, which are 3.2 ng.m^{-2}.h^{-1}, 11.1 ng.m^{-2}.h^{-1}, 7.2 ng.m-^{2}.h^{-1}, and 3.3 ng.m-^{2}.h^{-1} for forest site, farming field site, grass land and manmade forest site, water bodies. Total released time was estimated by assuming that natural emissions was emitted during summer time (i.e., 8 months from March to October for this case study in Chongquing, China) and during the day (i.e., 12 hours).

Global mercury emissions to the atmosphere from anthropogenic and natural sources suggests that emissions fluxes from lake surfaces is generally higher than the ocean surface (Pirrone *et al.*, 2009). In general, evasion of mercury from lake surfaces is not more than 2.39 ng.m^{-2}h^{-1} and that from ocean surface was 1.16-2.50 ng.m^{-2}h^{-1}. Dissolved mercury concentration in the top water micro layer is about 6.0ng/l. Mercury flux from soil was presented, i.e., -3.7 to 9.3 ng.m^{-1}h^{-1} for background site in the North America as well as other background site; 15.5 ± 24.2 ng.m^{-1}h^{-1} for alter geologic sites; 3334 ng.m^{-1}h^{-1} for the areas that calcine waste had been disposed of.

In Thailand, samplings of Hg concentrations in the near coastal area of Thailand have been monitored since year 1997 along the coastline of Thailand. The sampling was requested from the Pollution Control Department and it was figured that range of Hg concentration along the coastline was from 1.1 to 87.0 × 10^{-3} µg/l (equivalent to 1.1 – 87 ng/l), far less compare to 0.1 µg/l as in the National Coastal Water Quality Standard. However, monitoring in the coastal areas near industrial estates such as MapTaPhut and Laem Chabang Industrial Estates figured that Hg concentration is much closed to the maximum of National Standard, which is need to further investigation and study comprehensive about possible sources for good controllation. Hg concentrations in 16 major rivers (BangPaKong, Chao Phra Ya, Tha Chin, Mae Klong, Rayong, Phang Rat, Trad, Phetchaburi, Pran Buri, Lang Suan, Tapee, Pak Phanang, Tepa, Trang, Pattani, and Sai Buri) were sampled. It was found that during 1996 to 2000, total Hg concentration was about 0.05 to 1.5 µg/l which is smaller than standard of Thailand Surface Water Quality Standard of 2 µg/l were also measured by the PCD. Hg concentrations along Chaopraya river employed ultra clean technique combined with the atomic fluorescence figured that total Hg concentration from 0.024 to 0.133 µg/l.

In summary, according to local data, the total Hg concentration in Thailand is relatively low for both in land water and along coastal areas, therefore, a low range of EF flux was chosen for estimating Hg emissions from water surfaces.

A high deposition flux was found for Thailand case (by using a modeling approach) and high concentrations of soil near a coal-fired power plant was found, which suggested a similar level of pollution as in Chongquing province. Regarding to emissions from soil surface, EF from the study on China was chosen (Wang *et al.*, 2006) due to the more details compared to other sources. In addition, similar deposition map of Thailand and Chongquing province provided by global estimate (Pirrone and Keating, 2010). Since Thailand is in tropical country and the climate is hot and humid without winter, therefore, time release was set for whole year (12 months) which variation by monthly mean temperature (i.e., higher temperature the higher flux) and only 12 hour during day time. There is no natural emissions was released during night time.

Table 3.9: Emission Factors Used to Estimate Hg Emissions from Natural Sources

Source Type		**Release Flux ($ng.m^{-2}.h^{-1}$)**	**Reference**	**Release Duration**
Soil surface	Forest Land	3.2	(Wang *et al.*, 2006)	4380 hrs (equivalent to 12 hours of daytime/day and, 365
	Agricultural Land	11.3		
In-land Water Body		3.4		

3.3.2. Anthropogenic Source

3.3.2.1. Combustion Source

Hg emissions from combustion rely heavily on Hg content in fuel as well as on boiler configuration type. Hg content is generally high in low-level coal, followed by bio-fuel and oil accordingly. Coal used in Thailand is produced in Thailand or imported from nearby countries (i.e., Indonesia and Vietnam) and Hg contained in fuel are obtained from measurements (United Nation Environment Programme, 2011). The EF of combustion sources are well reported, mostly from sampling. The sources of emission factor are from database developed by US EPA or EEA, varied by fuel type, boiler configuration and emission control devices. In general, reported emissions factor do not provide speciation of Hg except some sources specific study (Lee *et al.*, 2004; Zhang *et al.*, 2008). Combustion technologies (i.e., boiler configuration and air pollution control devices) affect Hg transformation in the boiler and thus influence to Hg speciation and Hg reduction.

a) EFs for Estimating Hg Emissions from Combustion in Power Plants

A study on the estimation of anthropogenic emissions on a global scale proposed that the uncontrolled emissions factor for coal combustion is 0.1-0.3 $g.ton^{-1}$ for power plants and 0.3 $g.ton^{-1}$ for commercial boilers in industrial facilities (Pacyna *et al.*, 2010). For China's case, estimation of Hg emissions from coal fired emissions from power plant from bottom up approach (Streets *et al.*, 2005). Emissions from each source were estimated using sources specific information on coal content, boiler type (which define ratio of bottom ash and fly ash), as well as control equipment and efficiencies. The study investigate total 65 individual sources in this section, covering coal fired power plant, industrial used, residential use etc. 90% of coal fired power plant (mostly large power plant) use pulverized coal boiler while the rest is in stokers. About 50% of power plant equipped with ESP while the rest is wet particle scrubber and cyclones. For industrial, 90% of industrial facilities use stokers. Fluidized bed furnaces (FBF) are also share 8%. Cyclone and wet scrubber are two main types of PM control devices use on industrial boiler, contributing 61% and 28%.

Approximately 10% of industrial boilers are still without PM controls. Regarding to emissions control technology, there is also no specific equipment for Hg removal, however, conventional equipment for criteria pollutant is also have co-benefit for Hg removal and the efficiency is actually in wide range of uncertainties. ESP removed total Hg up to 30%, wet scrubber remove 10% and cyclones remove very less Hg. For combustion of other fuel such as fuel oil, gasoline, diesel and kerosene, bio fuel, average value of EF was used for the whole country. The value was listed in the following: 0.014, 0.058 and 0.020 g/ton for fuel oil combustion, gasoline, diesel and kerosene combustion, and bio fuel combustion.

For the case of Thailand, Hg content in coal was obtained from local study, which is an average of 0.12 g/ton for lignite, 0.27 g/ton for anthracite and 0.03 g/ton for bituminous and sub-bituminous (United Nation Environment Programme, 2011). The values originated from the range of Hg content in Thailand and nearby country that Thailand import coal such as Vietnam, Indonesia and Australia. Oil used in Thailand was extracted from the Gulf of Thailand, or imported refined and transported to factory. Hg content in the crude oil in the Gulf of Thailand is as high as 0.5931 g/ton, resulting that fuel oil used in boiler generally has Hg content is 0.0714 g/ton (Pollution Control Department, 2013). With the assumption that % of fly ash in oil fired power plant is 90% and control efficiency of Hg is 0%, resulting EFs of fuel oil is 0.06 g/ton, which is in range of 0.014 – 0.058 g/ton used in literature (Streets *et al.*, 2005). Value of 0.06 g/ton was used as controlled EFs for oil fired power plant in Thailand.

Thailand has air emission regulations. The emission limit for mercury from 'Infected Waste Incinerators' is 50 $\mu g/m^3$ and for any industrial emission source, the standard is 3 mg/m^3 for non-combustion systems and 2.4 mg/m^3 for combustion systems (PCD, 2012). The emissions limits is higher than would be expected for mercury concentrations in the flue gas of the average coal-fired power plant and no control action is likely to be taken (Sloss, 2012). Efficiency of emission control was selected based on the information from the EIA reports obtained from EIA surveys (Pham, 2007) for both coal fired power plant. In brief, power plants in Thailand use pulverized coal-fired boiler (PC) boilers for power plants with capacity are larger than 600 MW and use the combine ESP and FGD. Mixture of circulating fluidized bed (CFB) boiler and PC for medium to small power plants (MW is less than 600 MW) and the APCD is bag filter and cyclone for PM and limestone injection for SO_2. PM emissions control efficiency was up to 99%. The efficiency for Hg removal was obtained from measurement for lignite fired was 67% was used (Pollution Control Department, 2010) while for other coal fired power plants, average emission control efficiency of 40% was applied for coal fired power plants.

Biomass power plant uses fuels such as bagasse, husk as well as back liquor (from by-product from pulp and paper processes) or wood chips. Technology is stoker boiler; information was collected from EIA report. No emissions control was recorded for SO_2 while APCD for PM_{10} is the combination of multi cyclone and ESP or combination of multi cyclone and wet scrubber. It stated the PM efficiency is mostly more than 95%. Values of 0.007 g/ton as Hg content in all kinds of biomass fuel suggested by the UNEP Toolkit as global average value (Pollution Control Department, 2013). For China's case, the percent to bottom ash for stoker boiler is 17% while the rest is fly ash (Streets *et al.*, 2005). The EFs of biomass burning are estimated as products of Hg content in biomass and fractions of fly ash and emissions control efficiency. There is no emission control assumed for power plant use biomass. Details of EFs to estimating Hg emissions from power plants were shown in Table 3.9a.

b) EFs for Estimating Hg Emissions from Combustion in Industrial Facilities

Industrial facilities in Thailand use coal, oil, natural gas as well as biofuel. The Hg content of fuel (i.e., coal, oil al and biomass) was adapted from the UNEP Toolkit 2013. There is lack of information on technology equipped for industrial facilities use coal and biomass, though medium to large facilities in Thailand is needed to meet emissions standard of NOX, SO_2, and PM. Therefore, it is reasonable to assume that the technology and control efficiencies of coal and biomass is somewhat between 0% - 20%. In this work, value of 20% efficiency reduction was used for industrial facilities using coal and 0% efficiency was used for oil and biomass fired combustion. Information of combustion boiler technology for industrial facilities obtained from the DEDE provided in the Appendix A.

Details of EFs for estimating Hg emissions from industrial combustion were shown in Table 3.9b, because data on fuel type and fuel consumption of each single facility (of total 130,000 facilities) was not assessable; it was difficult to allocate emissions into a single facility. To do so roughly, information of installed power capacity and derived EF (g/HP) of each of 9 economic sectors was estimated using approach of Pham et al (2008) and briefly described here.

First of all, information of percentage share of energy (here, including different kind of fossil fuel, renewable fuel as well as electricity) used for each economic sector was estimated from governmental report (Department Of Alternative Energy Development And Efficiency, 2011) to get P_{energy}. Secondly, installed capacity (HP/hr) was converted to HP/year by multiplying with working schedule, representative for each 9 economic sector (hr/year) from literature review (Pham et al, 2007) to get HP_{year}. Thirdly, EF of each fuel type has unit conversion from (g/GJ) to (g/HP) using site specific calorific value (Department Of Alternative Energy Development And Efficiency, 2011) to get EFHP. Derived EF (g/HP) of each 9 economic sectors was obtained by multiplication of P_{energy} and EFHP, and Hg emissions of each facilities were products of derived EF (g/HP) and HP_{year}.

c) EFs for Estimating Hg Emissions from Combustion in Incinerator

The EFs of waste incinerators are influenced by Hg content in wastes and this is a source of uncertainty. Atmospheric EFs from waste incinerator in were reported from the UNEP Toolkit with value range from 0.9-9 g/ton (United Nation Environment Programme, 2011; Pollution Control Department, 2013), 1g/ton for global estimates (Pacyna *et al.*, 2010), and 2.8 g/ton for China (Streets *et al.*, 2005). Menhor (2010) reported Hg content in municipal waste to Ko Samui was ranging from 0.15 - 0.56 g/ton; resulting fly ash of Hg emissions was up to 0.1 - 0.4 g/ton (Muenhor, 2010). In additional, stack emissions standard of atmospheric Hg emissions of municipal waste incinerator are 0.05 mg/m^3. Using conversion factor from GAINS-Asia to convert mg/m^3 to g/ton for waste, EF of municipal waste incinerator is equivalent to 0.085 g/ton. Composition of municipal waste in Thailand has 3 major components which are listed here by order: organic waste, paper and plastic (Pollution Control Department, 2012) and based on current situation, waste such as electrical appliances, motors and spare parts, rubber tires and hospital wastes are not allowed to feed into the plant, resulting reasonable low atmospheric Hg emissions released.

EF from waste incinerators for medical and hazardous waste are 10 g/ton in Chingquong industrial provinces, China (Wang et al., 2006). The UNEP Toolkit suggested a value of 1-10 g/ton for waste in general (United Nation Environment Programme, 2011). Since waste in Thailand has been sorted and recycled partly before disposal and incinerated, lower bound value of Hg content should reflect the real situation in Thailand (Pollution Control Department, 2013), thus value of Hg content in coal of 1 g/ton was used in this work. In additional, stack emissions standard of atmospheric Hg emissions of industrial hazardous waste incinerators and infected medical waste show that value should not more than 0.1 mg/m^3 and 0.05 mg/m^3, respectively. Using conversion factor from GAINS-Asia to convert mg/m^3 to g/ton for waste, EFs of industrial waste incinerator and infected medical waste are equivalent to 0.17 g/ton and 0.085 g/ton, respectively. This value was reasonable due to industrial waste incinerators in Thailand use high technology in emissions reduction such as partial quench tower or evaporative cooling system, dry lime, activated carbon bag filter house, selective catalytic reduction and packed scrubber tower.

For EF from crematories, it is highly dependent on the consumption as well as the treatment method of Hg amalgams during dentistry treatments. Literature review reported that it is average 0.7 g of Hg emitted in a incinerated body (Pacyna et al., 2010). It was agreed with the Hg content in a body ranging from 1-4 g/body (United Nation Environment Programme, 2011). Therefore, EF of 0.7 g/body as generic value was used in this work.

Table 3.10: Emissions Factors Used to Estimate Hg Emissions from Combustion Sources

a) Power Plant

Emissions Sources	**Combustion Technology**[a]	**Hg content**[b] **(g/ton)**	**Air Pathway**[c] **(%)**	**Control Technology**[d]	**Control Efficiency**[e] **(%)**	**EFs**[f] **(g/ton)**
Lignite	Large plant Pulverized Coal-fired (Large plant)	0.12	99	FGD, ESP	67	0.039
	Stoker boiler (Small plant)	0.12	90		40	0.060
Sub Bituminous Coal	Circulating Fluidized	0.03	90	Low NOX burner, limestone injection, FF or Bag filter	40	0.016
Fuel oil		0.0714	90		-	0.06
Bio-fuel	Stoker boiler	0.007	83		-	0.006

a) Survey of combustion technology from the DEDE (Pham, 2007)

b) (United Nation Environment Programme, 2011)

c) (Streets *et al.*, 2005)

d) Survey of Environmental Impact Assessment (Pham, 2007)

e) (Pollution Control Department, 2010) and Pavlish (2009)

f) EF = Hg content x Air Pathway x Control Efficiency

Table 3.10: Emissions Factors Used to Estimate Hg Emissions from Combustion Sources

b) Industrial Facilities

Emissions Sources	**Combustion Technology**[a]	**Hg content**[b] **(g/ton)**	**Air Pathway**[c] **(%)**	**Control Technology**[d]	**Control Efficiency**[d] **(%)**	**EFs**[e] **(g/ton)**
Lignite	Lignite Boiler	0.12	90	PM Control[a]	20	0.09
Bituminous Coal	Coke Oven	0.03	90		20	0.02
Anthracite	Coke Oven	0.27	90		20	0.19
Other Coal	Coke Oven	0.12	90		20	0.09
Fuel oil	Not specific	0.0714	90		-	0.06
Bio-fuel	Not specific	0.007	83		-	0.006

a) Survey of Environmental Impact Assessment (Pham, 2007)

b) (United Nation Environment Programme, 2011)

c) (Streets *et al.*, 2005)

d) Results from survey of PM control technology in industrial coal fired boiler, referring that 60% of facilities does not equipped with effective control while other 40% quipped with medium control efficiency (40-50% Eff.) (Pollution Control Department, 2013)

e) EF = Hg content x Air Pathway x Control Efficiency

Table 3.10: Emissions Factors Used to Estimate Hg Emissions from Combustion Sources

c) Incinerators

Emissions Sources	**Standard Stack Emissions[a]**	**Conversion coefficient[b] $mg/m^3/(g/GJ)$**	**Net Calorific Value[c] (MJ/kg)**	**EFs[d] (g/ton)**
Municipal waste	0.05	2.86	4.86	0.085
Hazardous industrial waste	0.1	2.86	4.86	0.170
Medical waste	0.05	2.86	4.86	0.085
Crematoria	-			0.7 g/body

a) Thai Emissions Standard

b) Conversion coefficient for the case of waste (GAINS-Asia)

c) Obtained from DEDE (2012)

d) EFs (g/ton) = [net calorific value (MJ/kg) * standard stack emissions (mg/m3)]/conversion coefficient ($mg/m^3/(g/GJ)$)

3.3.2.2. Non-Combustion Process

a) EFs for Estimating Hg Emissions from Non-Combustion Processes in Cement Plants

Emissions factors to estimate the non-combustion of cement plants are described. In global estimation, Pacyna and co-author suggest EFs from cement is 0.1 g/ton (Pacyna *et al.*, 2006; Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008; Pacyna *et al.*, 2010). This factor is used to estimate atmospheric Hg emissions from cements for Asian country where lack of national estimate. This value was also used to estimated atmospheric emission for some specific region (Wang et al., 2006). US EPA (United State Environmental Pollution Agency, 1997) suggest average values 0.065 g/ton through measurement (include emissions from combustion of fossil fuel or hazardous waste as fuel). Streets and co-author (Streets et al., 2005) suggest value of 0.04 for the case of China (the value was modified from 0.065 g/ton mentioned above by subtracting energy intensity of 0.196 ton of coal per ton of cement produced from Chinese's local work).

The estimation of atmospheric emissions from cement industry in India calculated EFs using mass balance technique, accounting the use of coal during combustion and limestone as input; and value of 0.042 g/ton was reported (Mukherjee et al., 2009). UNEP Toolkit suggest that total Hg emissions emit to the environment (including air, water, land, products, general waste) are ranging from 0.02 - 0.2 g/ton for cement kilns without co-incineration of hazardous waste) and 0.08 - 0.8 g/ton for the case with hazardous waste. Of note that this input factor do not include emissions from combustion from fossil fuel combustion. With the distribution pathway to air pathway is 40% - 80% depending on emissions reduction devices, it can be derived that atmospheric emissions is ranging from 0.008 to 0.16 g/ton cement kilns without co-incineration of hazardous waste) and 0.032 - 0.64 g/ton for the case with hazardous waste (United Nation Environment Programme, 2011).

A local study employed the UNEP Tookit and using a mass balance technique (Pollution Control Department, 2013). In this study, materials used in the cement industry in Thailand are shale, limestone, marble, and gypsum. Hg content in such material was obtained from literature review (Johansen and Hawkins, 2003), i.e., 0.1 g/ton for shale, limestone, marl, and gypsum. Amount of material used in cement manufacturing are 4,126,822; 60,614,383; 69,000; and 33,020,472 ton for shale, limestone, marl, and gypsum, respectively. If consider those material alone, derived controlled EFs were 0.0065 g/ton, which are less compared to other values from literature.

In this thesis, a similar approach with the local study mentioned above was employed. Using the amount of cement production in year 2010 as 36,496,000 ton, derived EFs (g of total Hg emissions to all pathways/ton of cement production) is 0.0098 g/ton. This work also assumed that emissions to air pathway is up to 60%-70%, resulting derived EFs of atmospheric emissions are 0.0065 g/ton. However, cement plants in Thailand also use co-incinerator with hazardous waste and the amount of hazardous waste has been reported in year 2010 is 378,140 ton (as processing to be used as raw materials), accounting for 15.5% of total industrial waste management in year 2010 (total amount is 2,440,751 ton) (Pollution Control Department, 2012). Hg content in industrial hazardous waste is 1 g/ton (United Nation Environment Programme, 2011) and adapted in local estimate (Pollution Control Department, 2013), derived controlled EFs were 0.0127 g/ton, which is more comparable with value from literature. It should be noted that these EFs does not include emissions from coal combustion. Though it is well aware that there are combustion of coal as well as industrial hazardous waste in Thailand, however, atmospheric emissions due to fossil fuel combustion was estimated in emissions from sections of stationary combustion and incinerators. EF used in this thesis was 0.0127 g/ton for cement plant.

b) EFs for Estimating Hg Emissions from Non-Combustion Processes in Pulp and Paper Plants

Hg emissions exists in material input (wood), and fuel used (i.e. wood chip) in chemical recovery processes. Hg emission factor for chemical recovery process, from measurement from 8 recovery furnaces in the US, each controlled with an ESP, is 0.02 g/ton black liquor solids fired in the recovery furnace (United State Environmental Pollution Agency, 1997). This value was also introduced in the UNEP Toolkit (United Nation Environment Programme, 2011). Local study using UNEP Toolkit (Pollution Control Department, 2013) also recruited this EF to estimate Hg emissions from pulp and paper in Thailand. In Thailand, process of pulp and paper industry is Kraft process and PM10 emissions control was equipped using ESP alone or combination of cyclone, scrubber and EPS. Removal efficiencies of PM10 are ranging from 91% - 99%, obtaining from EIA surveys (Pham, 2007).

c) EFs for Estimating Hg Emissions from Non-Combustion Processes in Non-Ferrous Metal Production

Non Ferrous Metal, including Zn, are varied from country by country. For the case of China, it was 13.8–156.4 g/ton with country average value 86.6 g/ton (Streets et al., 2005). Pacyna and co-authors suggest value of 7.5-8.0 g/ton of Zinc production (Pacyna et al., 2006) and adjust to 7.0 g/ton (Pacyna et al., 2010) or value of 25 g/ton in India estimates (Mukherjee et al., 2009). UNEP Toolkit suggests value of 1-20 g of Hg per ton of ore mined (United Nation Environment Programme, 2011), which is equivalent to 5.8 -115.6 g/ton for the case of Thailand. Though there was no measurement on sources available for the public, Zinc factory in Thailand was equipped well with environmental value, therefore, value of 5.8 g/ton was used in this work.

d) EFs for Estimating Hg Emissions from Non-Combustion Processes in Large Scale Gold Mining

Emissions on a large scale gold mining are quite uncertain and there are several values that use to estimate emissions from this source. The EF is 0.04 g/ton of gold ore was suggested by UNEP Toolkit 2011 or 0.5 g/g gold product in Pirrone (2010) and 0.025-0.027g/g of gold product in Pacyna (2010). In Thailand, the technology of large scale gold production was cyanide process which was no Hg process involved. Therefore, the value of 0.025 g/g of gold produced was used for this study.

Table 3.11: Emissions Factors Used to Estimate Hg Emissions from Non-Combustion Processes

Emissions	EFs	Ref.
Gold (large	2.5 x 10^{-2} g/g gold ore	(Pacyna *et al.*, 2010)
Zinc	7 g/ton of zinc product	(Pacyna *et al.*, 2010)
Cement	6.5 x 10^{-3} g/ton cement (for non-hazardous material) or 12.7 x 10^{-3} g/ton cement (for hazardous material)	(Pollution Control Department, 2013)
Pulp and Paper	2 x 10^{-2} g/ton of black liquor	(Pollution Control Department, 2013)

3.3.3. Biomass Open Burning

Hg EFs from biomass open burning is customarily estimated using ratios of ambient CO/Hg from different locations (Friedli *et al.*, 2003). Ratio of CO/Hg is approximately 10^{-7}. Most of the experiences were located in the United State and limited of measurement was conducted in Asia. Most of measurement were for wild fires and limited for agricultural waste. In this work, EF for forest and agriculture, obtained from literature review (Friedli *et al.*, 2003), are presented in Table 3.11.

Table 3.12: Emissions Factors Used to Estimate Hg Emissions from Biomass Open Burning (Friedli *et al.*, 2003)

Emission Sources	EFs
Forest	0.113 g/ton
Agricultural residue	0.037 g/ton

3.3.4. Method to Assess Speciation Distribution of Emissions

While most emission factors reported in the literature review were reported as total Hg emissions, the share of Hg speciation is important to understanding the transport and fate of Hg in the atmosphere due to each Hg species. The speciated Hg emissions varied by emitted condition (i.e., material input, processes as well as emission control devices). For single sources, Hg speciation can be obtained through measurement, whether at each processes and at the final released from stack using Ontario Hydro (OH) method and US EPA 101A (Lee *et al.*, 2004; Lei *et al.*, 2007; Niksa and Fujiwara, 2009).

In general, fuel characteristics such as chlorine content and ash composition, and operational conditions affect Hg speciation and transformation during combustion processes. In addition, coal composition, boiler configuration and APCD has significant affected to reduce Hg amount and change the proportion of Hg speciation in the exhaust gas to the stack. Before entering to APCD, Hg speciation depends on coal composition and boiler configuration. ESP/EF has high efficiency to remove emission related to particulate matter, thus also present high efficiency to reduce Hg^P while FGD has high efficiency to reduce Hg^{2+} due to its high water soluble capacity.

In Thailand, though measurements of Hg emissions from large stationary combustion's boiler stack were available, there was no information on Hg speciation. In the regional model approach, where aggregated sources need to be considered, the default speciation suggested by global estimation was firstly used and added up with speciation value from foreign studies to fill gaps in the case of missing information in the global default. In Table 3.13, speciation profiles used in this work are presented.

Table 3.13: Speciation Profiles of Hg Emissions

Emissions Sources	**Fraction[a] of Hg^T**		
	Hg^0	**Hg^{2+}**	**Hg^P**
Combustion emissions from power plants	0.5	0.4	0.1
Combustion emissions from residential heating	0.5	0.4	0.1
Combustion emissions from industrial/commercial/residential boilers	0.5	0.4	0.1
Pig iron and steel production	0.8	0.15	0.05
Secondary steel production	0.8	0.15	0.05
Non-ferrous (Cu, Zn, Pb) metal production	0.8	0.15	0.05
Large-scale gold production	0.8	0.15	0.05
Mercury production	0.8	0.2	0[b]
Cement production	0.8	0.15	0.05
Chlor-alkali industry(caustic soda production)	0.7	0.3	0[b]
Waste incineration	0.2	0.6	0.2
Cremation emissions	0.8	0.15	0.05
Artisanal and small-scale gold mining	1	0[b]	0[b]
Grassland savanna burning[c]	0.96	0[b]	0.04
Forest burning[c]	0.96	0[b]	0.04
Waste and residue burning[c]	0.96	0[b]	0.04

a) (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008) unless noted

b) Zero

c) (Streets et al., 2005)

3.4. Results and Discussions

3.4.1. Emissions Estimate by Source Category

3.4.1.1. Amount of Atmospheric Hg Emissions from Natural Sources

Emissions from soil and water surfaces are presented in Table 3.14. As seen, soil emissions from farming field and forest share the largest contribution (i.e., 82.8% and 16.3%, respectively), followed by soil emissions from forest of total natural Hg emissions while Hg emissions from water surfaces is less significant (i.e., 1.2%). Literature review show that Hg emissions from natural sources are in Hg^0 form.

Table 3.14: Hg Emissions from Natural Sources in Thailand Year 2010

Source type		Emissions (kg)
Soil surface	Forest	2,635.0
	Agricultural land	13,373.5
In-land Water Body		189.0
Total		16,197.5

3.4.1.2. Amount of Atmospheric Hg Emissions from Anthropogenic Sources

a) Combustion Source

Amount of Atmospheric Hg Emissions from Power Plants

In year 2010, atmospheric Hg emissions from the power sector were 851.5 kg. It is noted that even though fuel consumption in this sector was significant as compared to other sources, fair-high emissions control efficiency helped to reduce its final emissions. By fuel, coal and lignite fired power plants emitted up to 92.3%, biomass fired power plant emitted 7.4% and the rest were from oil and diesel fired power plants combined. Using the fact that population of Thailand in 2010 was 65.98 million (NSO, Executive summary, 2012) and electricity generation in 2010 was 159,518 Gwh (DEDE, Electricity in Thailand, 2012), derived indirect emission emitter of atmospheric Hg in Thailand due to power generation is 10.5 µg/capita or 4,333 µg/Gwh. In terms of Hg speciation in this source, a fair comparable fraction between Hg^0 and Hg^2 was found, sharing fairly contributions for both deposition near sources and outflow. In addition, from thermal power plants, where atmospheric emissions were released through a stack height above 100-200 meters, suggesting possibility of long range transport of Hg emissions.

Table 3.15: Hg Emissions from Power Generation in Thailand Year 2010

a) Power Generation- EGAT and IPP

Region	**Sector**	**Diesel oil**	**Fuel oil**	**Coal**	**Lignite**	**Total**
Central	EGAT	0.1	0.3	-	-	0.4
	IPP	-	-	-	-	-
Eastern	EGAT	0[a]	0.7	-	-	0.7
	IPP	-	-	53.9	-	53.9
Northern	EGAT	0.4	-	-	627.4	627.8
	IPP	-	-	-	-	-
Northeastern	EGAT	0[a]			-	
	IPP				-	
Southern	EGAT	0.1	0.9	-	-	1.0
	IPP	-	-	-	-	-
Total		0.6	1.8	53.9	627.4	683.8

a) 0[a]: Less than 0.05

Table 3.15: Hg Emissions from Power Generation in Thailand Year 2010

b) Power Generation- SPP and VSPP

Fuel	**Sub-fuel**	**Emissions (kg)**
Lignite & Coal		
	Coal	101.8
	Lignite	2.5
Oil		0[a]
Renewable		
	Paddy Husk	13.9
	Bagasse	28.9
	Agricultural Waste	20.1
Total		167.7

a) Less than 0.05

Amount of Atmospheric Hg Emissions from Industrial Facilities

Hg emissions from industrial combustion in year 2010 were 1,445.4 kg. Among 9 economic sectors: Chemical and Basic Metal industries had highest coal consumption while Food & Beverage and Non-Metal Industry had the highest bio-fuel consumption (Department of Alternative Energy Development and Efficiency, 2011) explaining relatively high emissions in these sectors. In this sector, comparable fraction of Hg^0 and Hg^{2+} are found, sharing fair contributions for both deposition near sources and outflow.

Table 3.16: Hg Emissions from Combustion in Industrial Facilities in Thailand Year 2010

Sector	**Emissions (kg)**								
Fuel	**Food and beverages**	**Textiles**	**Wood and furniture**	**Paper**	**Chemical**	**Non-metallic**	**Basic metal**	**Fabricated metal**	**Others**
Coal & its products	2.0	1.2	0[a]	14.1	221.7	858.1	64.6	0[a]	117.6
Bituminous	0[a]	0.1	0[a]	2.8	0.3	17.1	0[a]	0[a]	0[a]
Anthracite	0[a]	0[a]	0[a]	0[a]	0[a]	19.4	28.2	0[a]	0[a]
Coke	0[a]	0[a]	0[a]	0[a]	0[a]	0.0	23.4	0[a]	0[a]
Lignite	2.0	1.0	0[a]	9.8	2.0	286.4	0.0	0[a]	0[a]
Briquettes & other coal	0[a]	0[a]	0[a]	1.5	219.4	535.2	13.0	0[a]	117.6
Petroleum product	0[b]	0[b]	0[b]	0[b]	0[b]	0[b]	0[b]	0[b]	0[b]
Renewable energy	140.3	0[a]	0.8	0[a]	5.7	19.0	0[a]	0[a]	0[a]
Fuel wood	4.7	0[a]	0.2	0[a]	1.4	2.1	0[a]	0[a]	0[a]
Agricutural waste	30.8	0[a]	0.6	0[a]	4.3	16.6	0[a]	0[a]	0[a]
Paddy husk	16.7	0[a]	0[a]	0[a]	0[a]	0.3	0[a]	0[a]	0[a]
Bagasse	88.2	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]	0[a]
Total	142.4	1.2	0.8	14.1	227.4	877.1	64.7	0[b]	117.7

a) Zero

b) Less than 0.05

Amount of Atmospheric Hg Emissions from Incinerators

Atmospheric Hg emissions from incinerators in year 2010 were 327.5 kg. As expected, they were mostly from crematories (up to 76.2%), municipal waste and hazardous waste (approximately 11% for each). High Hg emissions were found in crematories due to a previous assumption that there was no effective Hg control. In contrast, low Hg emissions due to hazardous waste incinerator and medical waste incinerator due to strict regulation that emissions at stack cannot be exceed 0.05 mg/m^3 In this sector, relatively high fraction is from Hg^0 was emitted in elevated level of stack resulting a possibility to have long range transport. In regional distribution, emissions from municipal waste located in the Southern of Thailand. Emissions of medical waste were high in the Central and Northeastern regions and emissions of crematories were high in the Northeastern, Central and Northern regions.

Another source under this sector is informal waste burnings, which have been recorded nearby suburban or forest areas. This could result in high potential emissions; however, due to lack of reliable information, the emissions were not included here. According to the authors' best guess, emissions magnitude of this source is possible up to 1,000 kg.

Table 3.17: Hg Emissions from Combustion in Incinerators in Thailand Year 2010

Emission Sources	Emissions (kg)
Municipal Waste	7.8
Medical Waste	3.5
Hazardous Waste	83.9
Crematories	232.3
Total	327.5

b) Amount of Atmospheric Hg Emissions from Non-Combustion Processes

Table 3.18 below presents emissions from industrial processes. Within Hg emissions from industrial processes, zinc production and cement production have high contributions with 59.6% and 23.5%, respectively due to large amounts of industrial production in Thailand. Hg emissions from large scale gold production are expected to increase in the near future due to the extension of plants' capacity (United States Geological Survey, cited 2011). In this sector, fraction of Hg^0 is dominant (i.e., 80%), however, emissions are emitted in near ground level; therefore, it has insignificant contribution to emissions outflow.

Table 3.18: Hg emissions from Industrial Processes in Thailand Year 2010

Emission Sources		Emissions (kg)
Metal	Gold (large scale)	103.1
	Gold (amalgam)	-[a]
	Zinc	849.5
	Cement	462.8
Mineral	Pulp and Paper	10.2
Total		1,425.60

a) An investigation of gold extraction using amalgam method is conducted in year 2007 in Phanom Pha Gold Mine, Phichit Province, Thailand and annual amount of Hg emissions from this activity was 11.0 kg (Pataranawat, 2007)

3.4.2.3. Amount of Atmospheric Hg Emissions from Biomass Open Burning

It was found that in 2010, Hg emissions from biomass were 247.6 kg, of which 94.5% was contributed by forest fires. Biomass emissions were found to be dense in the Northern and Northeastern regions of Thailand and high during January to April. Details are shown in Table 3.19 below

Table 3.19: Hg Emissions from Biomass Open Burning in Thailand Year 2010

Type		Emissions (kg)
Forest	Mixed Deciduous Forests	95.6
	Deciduous Dipterocarp Forests	50.8
	Other Forests	87.7
Agriculture	Paddy Fields	9.3
	Corn (or Maize)	3.1
	Sugarcane	1.2
Total		247.6

3.4.1.4. Total Atmospheric Hg Emissions in Thailand Year 2010

Total atmospheric Hg emissions in year 2010 were 20,495.2 kg, of which 79.0% were from natural sources, 19.7% from anthropogenic sources, and 1.2% from biomass open burning. Within Hg speciation, Hg^0, Hg^{2+} and Hg^P accounted for 91.7 %, 6.5%, and 7.8 % respectively. Though it is needed further quantitatively investigation by atmospheric modeling, relatively high percentage of Hg^0 (a species with 0.5 to 2 year atmospheric lifetime) somehow indicates that Hg emissions in Thailand has high potentially exported to out of the country.

In year 2010, the total Hg emissions from anthropogenic sources were ranged 4,050.1 kg, which were attributed from combustion sources (i.e. 64.6%), industrial processes (i.e., 35.4%). In particular, under internal combustion thermal power plants contributed for 32.6%, industrial combustion accounted for 55.3%, and incinerators with 12.1%; under industrial processes, cement industry accounted for 32.5%, zinc industry accounted for 59.6%, and pulp and paper industry with 0.7%. In year 2010, total Hg emissions from biomass burning were 247.6 kg, forest fires contribute up to 94.5% and agricultural waste contributed 5.5%.

Table 3.20: Hg Emissions and Speciation in Thailand Year 2010

a) Natural Sources

Sources	**Emissions**			
	Hg^T (kg)	**Hg^0 (kg)**	**Hg^{2+} (kg)**	**Hg^P (kg)**
Soil	16,008.5	16,008.5	0[a]	0[a]
Water	189.0	189.0	0[a]	0[a]
Total	16,197.5	16,197.5	0[a]	0[a]

a) Zero

Table 3.20: Hg Emissions and Speciation in Thailand Year 2010

b) Anthropogenic Sources

Sources		**Emissions (kg)**			
		Hg^T	**Hg^0**	**Hg^{2+}**	**Hg^P**
Combustion – Thermal power plants					
	Coal	155.7	77.9	62.3	15.6
	Lignite	629.9	315.0	252.0	63.0
	Fuel oil & Diesel oil	2.5	1.3	1.0	0.3
	Bio-fuel	62.9	31.5	25.2	6.3
Combustion - Industrial facilities					
	Coal	978.1	489.1	391.2	97.8
	Lignite	301.4	150.7	120.6	30.1
	Fuel oil	0.2	0.1	0.1	0.0
	Biofuel	165.8	82.9	66.3	16.6
Combustion - Incinerators					
	Household waste	7.8	1.6	4.7	1.6
	Hazardous industrial waste	83.9	16.8	50.4	16.8
	Medical waste	3.5	0.7	2.1	0.7
	Crematoria	232.3	185.9	34.9	11.6
Process - Industrial facilities					
	Metal – Zn	849.5	679.6	127.4	42.5
	Metal – Au (large scale)	103.1	82.5	15.5	5.2
	Cement	462.8	370.2	69.4	23.1
	Pulp and paper	10.2	8.2	1.5	0.5
Total		4,050.1	2,493.9	1,224.6	331.6

b) Less than 0.05

Table 3.20: Hg Emissions and Speciation in Thailand Year 2010

c) Biomass Burning

Sources	**Hg^T (kg)**	**Hg^0 (kg)**	**Hg^{2+} (kg)**	**Hg^P (kg)**
Forest	271.3	260.5	0^a	10.9
Agricultural residue	8.3	8	0^a	0.3
Total	279.6	268.5	0^a	11.2

a) Zero

Table 3.20: Hg Emissions and Speciation in Thailand Year 2010

d) Priority Sources of Hg Emissions from Anthropogenic Sources

No	**Sources**		**Emissions (kg)**			
			Hg^T	**Hg^0**	**Hg^{2+}**	**Hg^P**
1	Combustion - Industrial facilities	Coal	978.1	489.1	391.2	97.8
2	Process - Industrial facilities	Metal – Zn	849.5	679.6	127.4	42.5
3	Combustion – Thermal power plants	Lignite	629.9	315.0	252.0	63.0
4	Process - Industrial facilities	Cement	462.8	370.2	69.4	23.1
5	Combustion – Industrial facilities	Lignite	301.4	150.7	120.6	30.1
6	Combustion - Incinerators	Crematories	232.3	46.5	139.4	46.5
7	Combustion - Industrial facilities	Biofuel	165.8	82.9	66.3	16.6
8	Combustion – Thermal power plants	Coal	155.7	77.9	62.3	15.6
9	Process - Industrial facilities	Au production (large scale)	103.1	82.5	15.5	5.2

3.4.1.4. Uncertainties of Estimation of Atmospheric Hg Emissions in Thailand Year 2010

Though it is difficult to provide exact uncertainty range due to lack of data, current estimates have uncertainties for the following reasons: (1) emissions factor (e.g., emissions factor chosen from local study or adapted values from foreign studies may come from single measurement which may not exactly representative for all the cases of Thailand), and (2) emissions reduction technology and its efficiency (i.e., due to lack of information on APCD's reduction efficiencies, values of efficiency in this work were adapted from literature review). Among sources, emissions from combustion from thermal power plants and industrial facilities are quite high certain while those from incinerators, metal extraction are low certain due to lack of data on Hg containing in waste and material input, respectively.

In addition, the Hg emissions inventory developed in this study was among one of the first local efforts for Hg emissions inventory in Thailand covering all anthropogenic sources. To roughly evaluate quality of the development, magnitude of Hg emissions from this study has been compared to other studies, one of them was international (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008). It was developed in global scale for year 2005 using top-down approach to provide the understanding of Hg emissions in global scale and for modeling input. Details of comparison are shown in Table 3.21 below. There are a number of possible reasons contribute to differences (e.g., different emissions factors and activity data sources). In particular, our estimate was lower than that of literature due to some of Hg emissions sources have been no longer exist (for example, caustic soda industry has shifted to non-Hg technology by year 2005) and we have applied far to high emissions control efficiency to some major sources (for instance, coal fired combustion).

Table 3.21: Comparison between Hg Emissions of Selected Anthropogenic Sources in This Work and Literature Review

Anthropogenic Emission Sources	**UNEP (Arctic Monitoring and Assessment Programme/United Nation Environment Programme, 2008)**		**This Estimate**
	Base year 2005	**Projection 2020**[a]	**Base year 2010**
Stationary combustion[b]	6,083.5	3,947.9	2,624.5
Non-ferrous metal production	576.0	208.6	849.5
Pig iron and steel production	212.0	76.8	0[c]
Cement production	3,032.0	1,334.4	462.8
Large-scale gold production	177.2	177.2	103.1
Caustic soda production	0[d]	0[d]	0[d]
Other industrial processes	0[d]	0[d]	10.2[e]
Total	10,080.7	5,744.9	4,050.1

a) Projection to year 2020 under "Extended Emissions Control Scenario", where emissions control technologies currently used in Europe and the USA are used elsewhere. This would include control technologies, such as ESP or bag houses and FGD, systems on coal combustion systems (Pacyna *et al.*, 2010).

b) Includes combustion in power plants, industrial facilities and incinerators.

c) Summation of Hg emissions from Zinc mining and production

d) Zero

e) Pulp and paper

3.4.2. Spatial Distribution of Atmospheric Hg Emissions Characteristics

As presented in Figures 3.5 – 3.7 below, emissions distributed in Thailand were not even for the entire country. For natural sources, Hg emissions were high in the northeastern, the eastern and southern regions due to a release of Hg emissions from agricultural soil surface. In addition, Hg emissions were also significant in the northern regions, due to a release of Hg emissions from forest soil. Hg emissions from water surface were no significant and mostly located in the central region. For anthropogenic sources, Hg emissions were located mostly in the central and eastern regions due mostly to high operational power plants, industrial facilities and incinerators in these 2 regions. For biomass open burning sources, Hg emissions from forest open burning were mostly located in the upper northern regions while Hg emissions from agricultural waste burning were located mostly in the northeastern and lower northern regions.

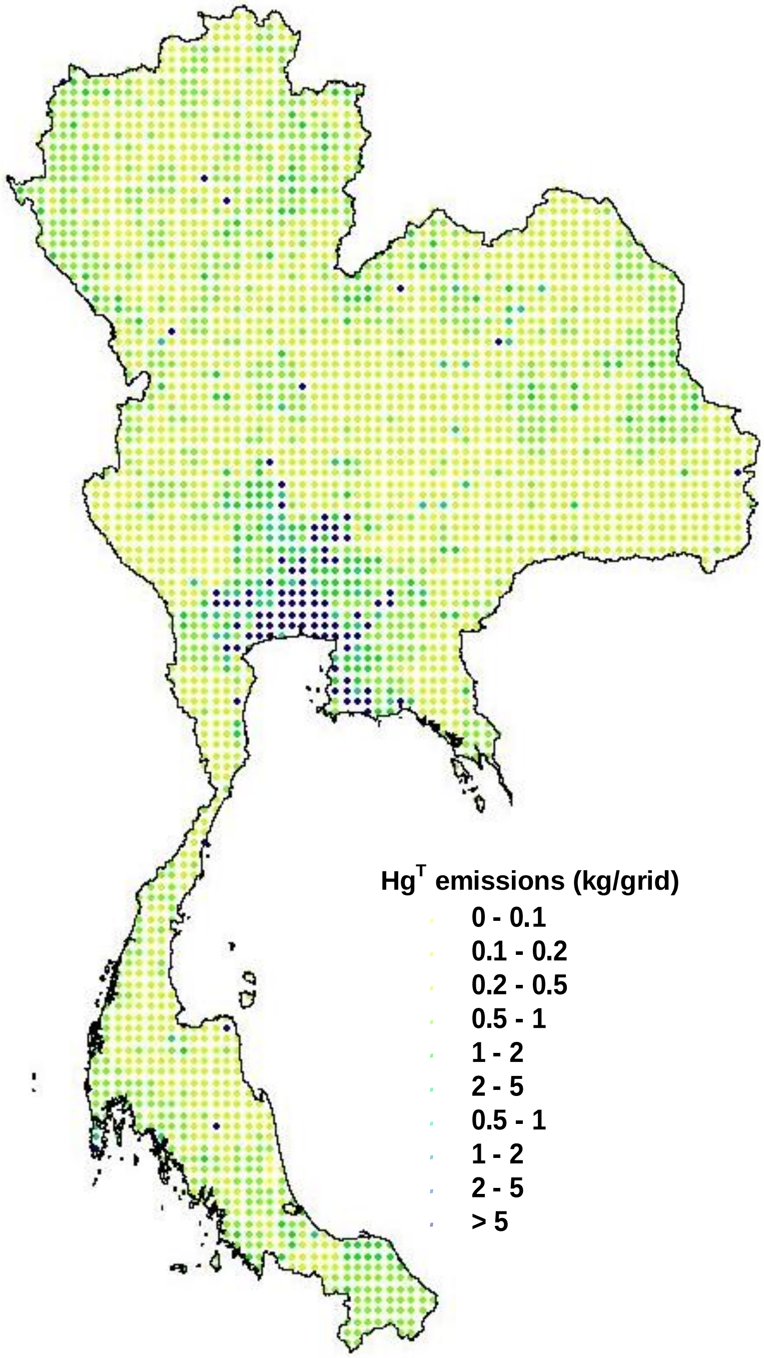


Figure 3.1: Map of Anthropogenic Atmospheric HgT Emissions in Thailand

3.5. Chapter Summary

In this chapter, atmospheric Hg emissions in year 2010 have been characterized, using a bottom-up approach. Source specific activity data were collected locally and emissions factors were either from local sources or adapted from literature review with proper adjustments to well reflect emitting behaviors of various sources in Thailand. Bottom up approach was used for estimating Hg emissions from power sector while semi bottom up approach was used for other sources. It was found that in year 2010, total atmospheric Hg emissions in year 2010 were 20,495.2 kg, which 79.0% from natural sources, 19.7% from anthropogenic sources, and 1.2% from biomass open burning. Within Hg speciation, Hg^0, Hg^{2+} and Hg^P accounted for 91.7 %, 6.5%, and 7.8 % respectively. Uncertainties of this work are mostly from the uncertainties from the selection of emission factor (as function of Hg content and emissions control devices equipped). Among sources, emission estimates from combustion, especially from power plants were most certain while those from industrial processes are most uncertain and should be improved in future work. Local developed EFs and more shared information from stake holders on plant's site specific information are desired to reduce the source of uncertainties. The findings mentioned above provide characteristics of atmospheric Hg emissions in Thailand and are sufficient to serve for emission input of Hg species for an air quality model.

CHAPTER 4

MODELING OF METEOROLOGICAL INPUTS TO AIR QUALITY MODEL

This chapter presents the theories and the methodology used in investigating air mass transportation, which is the key input to air quality model. Several sensitivity options in meteorological model are tested to choose the best suitable option for deposition study in Thailand. Expected outputs are meteorological parameter for interest period (i.e., Feb, May, August, and November) which is ready to process to air quality model's input.

4.1. Description of MM5

4.1.1. Principle of MM5

In this study, the fifth generation Pennsylvania State University (PSU)/National Centers for Atmospheric Research (NCAR) Mesoscale Model (MM5) (Grell et al., 1994; Dudhia et al., 2002) is employed. It is non-hydrostatic, limited-area, and uses the terrain following sigma coordinate. The non-hydrostatic define constant reference states and perturbations as E.q. 4.1 in the following:

$$\begin{aligned} p(x,y,z,t) &= p_o(z) + p'(x,y,z,t) \\ T(x,y,z,t) &= T_o(z) + T'(x,y,z,t) \\ \rho(x,y,z,t) &= \rho_o(z) + \rho'(x,y,z,t) \end{aligned} \qquad \textbf{(E.q. 4.1)}$$

where

p pressure p_o reference state pressure p' perturbation pressure

T Temperature T_o reference state temperature T' perturbation temperature

ρ Density of air ρ_o reference state density ρ' perturbation density

Each model level is defined at a value of σ, where σ values are zero at the top of the model and one at the model's surface, which is defined in terms of pressure as follows:

$$\sigma = \frac{\rho_o - \rho_t}{\rho_s - \rho_t} \qquad \textbf{(E.q. 4.2)}$$

Where

ρ_s Pressure at surface

ρ_t Pressure at top

The MM5 model incorporates many options for physical parameters. In this study, three key physical parameters: cumulus parameterizations (CPs), planetary boundary layer (PBL) parameterizations, and land surface models (LSMs) are selected for sensitivity testing.

4.1.2. Input Requirements (to Input in MM5)

In order to run MM5 for a specific domain during a particular time, fixed data includes topography data, vegetation type and land use classification, while variable data input include atmospheric data (obtained from global analysis data), water temperature, cloud and precipitation (initial mixing ratio) (USEPA/OAQPS, 2002).

4.1.3. Outputs As Inputs in Air Quality Model

Direct outputs of MM5 contain information of hourly meteorological parameters for the interested resolution (here are 36 km and 12 km in this work). MM5 outputs are needed to be converted to be properly input to the air quality model (Otte and Pleim, 2010) (in particular, wind parameter are need to be translated from Arakawa "B" configuration in MM5 to Arakawa "C" configuration in most of air quality model, including CAMx).

4.2. Methodology

4.2.1. Meteorological Domain

Meteorological domains are set to capture the effects of wind to Thailand. The coarse domain covers the SE Asia and parts of China and India, consisting of 17424 cells with a grid size 36 x 36 km^2. The finer domain covers Thailand, consisting of 20736 cells with a grid size 12 x 12 km^2. The meteorological simulations are proposed as use for one-way nesting grids, with a nesting ratio 3:1, and 23 vertical layers (Tables 4.1 and 4.2). The study domain is in

Lambert conformal projection centered at Bangkok (i.e., 13.5° N and 100.5° E) (see Figure 4.1).

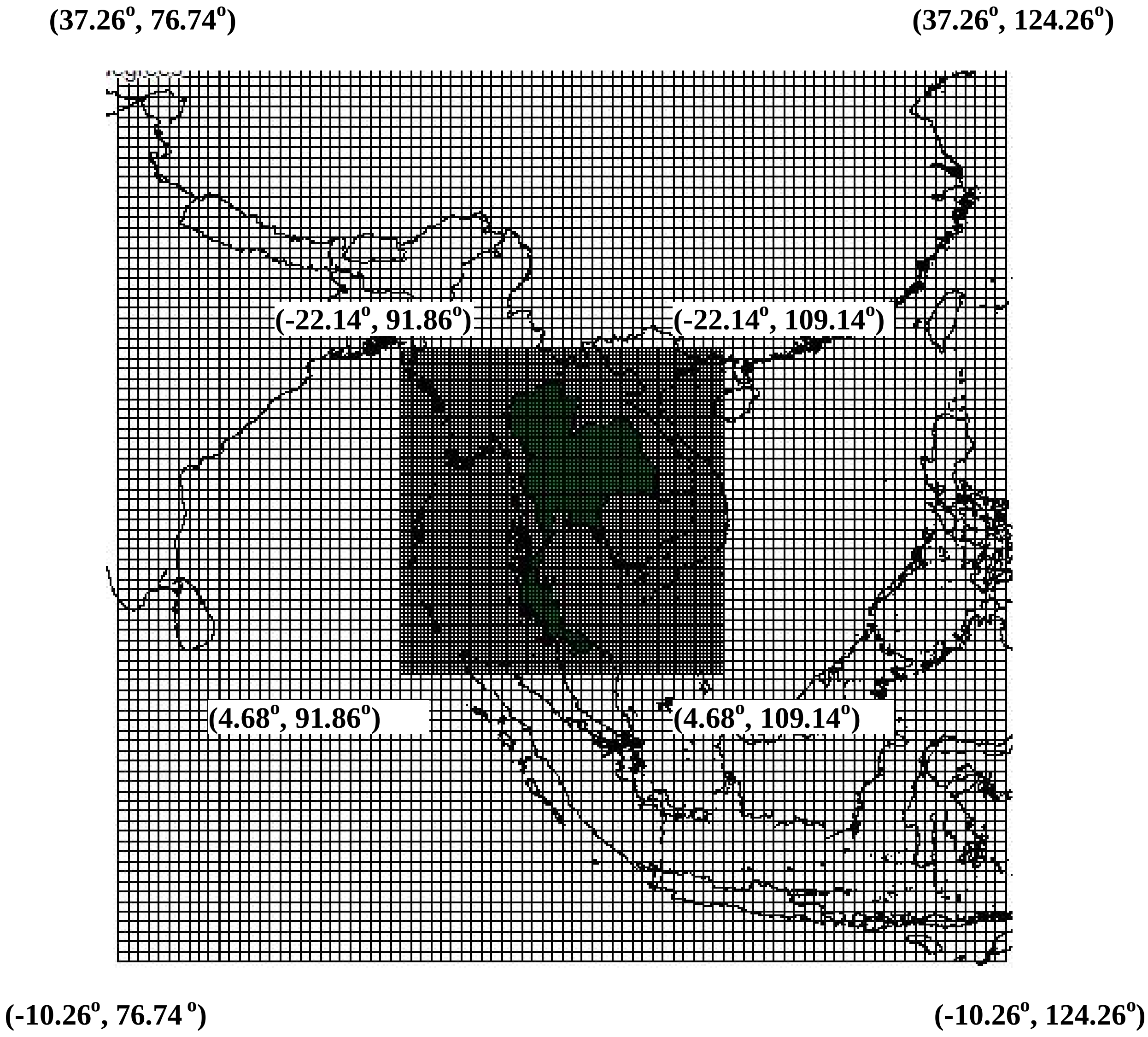


Figure 4.1: Modelling Domain of the Work

Table 4.1: MM5 Domain

Domain #	**Map Projection**	**Grid Size (km)**	**Vertical Level**	**Grid Number**	**Mother Domain I, J**	**Terrain Resolution (km)**
Domain 1	LCP[a]	36	24	132, 132		19
Domain 2	LCP[a]	12	24	169, 145	37,43	9

a) Lambert Conformal Projection

Table 4.2: Vertical Layers Used in MM5

No.	Full/Half Sigma	Height (m)
23	0.000	14,649
22	0.020	13,855
21	0.050	12,810
20	0.100	11,346
19	0.200	9,058
18	0.300	7,277
17	0.400	5,807
16	0.500	4,549
15	0.600	3,445
14	0.650	2,940
13	0.700	2,460
12	0.750	2,003
11	0.800	1,568
10	0.850	1,152
9	0.900	752
8	0.950	369
7	0.975	183
6	0.980	146
5	0.986	102
4	0.990	73
3	0.993	51
2	0.996	29
1	0.998	14
	1.000	Ground

4.2.2. Work Flow And Data Preparation

Work flow of MM5 is shown in Figure 4.2 below. Description of workflow as well as data preparation is described

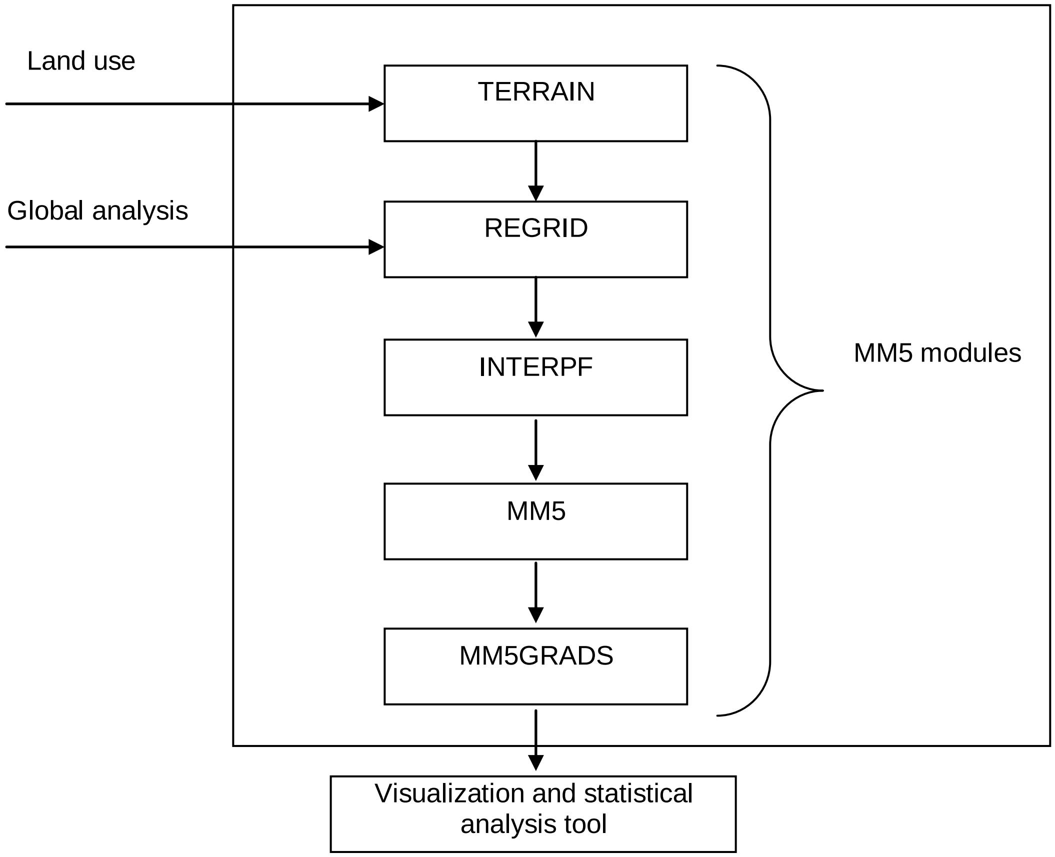


Figure 4.2: Work Flow of the MM5 Meteorological Model (UCAR, 2008)

4.2.2.1. TERRAIN

The TERAIN module lets the user design domains. In this study, there are 2 domains with 2 ways nesting option. Output of this module includes TERRAIN_DOMAIN 1 and TERRAIN_DOMAIN2 which are served as input for INTERPF module. A 30-second elevation dataset of topography from the global survey and vegetation data are from United State Geological Survey / Global Land Cover Characterization (USGS/GLCC) (http://edc2.usgs.gov/glcc/glcc.php).

4.2.2.2. REGRID

The REGRID module interpolates global analysis data FNL from 1^{o} (i.e., 108 km) to the grid resolution of this work (i.e. 36 km and 12 km). The initial and lateral boundary conditions were provided by the National Center for Environmental Prediction (NCEP), and the National Center for Atmospheric Research (NCAR) with a global resolution 1.0 x 1.0 degree (this data is available online: http://www.cdc.noaa.gov). Sea Surface Temperature (SST) from Real Time Global (RTG) has a 0.5-degree resolution (this data is available online: http://polar.ncep.noaa.gov/sst/ophi/). NCEP reanalysis and SST data were analyzed and then interpolated to the model grid for the preparation of initial and lateral boundary conditions

4.2.2.3. INTERPF

This program takes pressure-level meteorological fields produced either by REGRID, and interpolates pressure level data to sigma levels, which are defined by users (for this study, vertical levels are presented in Table 4.2). In this work, there are total unequally spacing 22 layers which denser within the boundary layer in order to capture meteorological parameters within the boundary layer, which provide important information for transformation of emissions in this layer.

4.2.2.4. MM5

The core module MM5 allows the user to choose the physical options of the simulation. In this modules, physical options of MM5 such as cumulus parameterizations (CPs), planetary boundary layer (PBL) parameterizations, and land surface models (LSMs) are chosen.

4.2.2.5. Visualization/Analyzing Tool

Meteorological observation data was collected from the Thai Meteorological Department, including temperature, wind speed, wind direction, relative humidity, precipitation, solar radiation, pressure etc. In this study, several statistical software packages were examined to evaluate MM5 output. They are described as follows:

1) METSTAT: METSTAT is developed by ENVIRON as a supporting software package for CAMX (downloaded from http://www.camx.com/download/support-software.aspx). METSTAT provide quick statistical evaluation of MM5 for 4 parameters: wind speed, wind direction, temp, and humidity. The software work well under condition that user need to provide more than 3 dataset from meteorological station.

2) Readv3: One of the MM5 utilities that MM5 provided to the user. This software provide time series of up to 10 parameters defined by users, but users need to calculate statistic manually, and

(3) GRADS: This software package can be used for both statistical and (mostly) graphical evaluation of MM5 output. It employs a package called MM52GRADS to convert MM5 results to be readable form by visualization tool, here is GRADS. At this step, user can choose frequency of converted output as well as 2D and 3D meteorological parameters to be viewed by GRADS.

4.2.3. Experiments Conducted in this Study

4.2.3.1. Purpose of the Experiments

As one of the key inputs for air quality modeling, the robustness of meteorological outputs is crucial in assessing the fate of emissions. Meteorological parameters such as wind speed, wind direction, temperature, and radiation highly contribute to uncertainties of air quality model. These uncertainties can be much reduced if the applications choose appropriate physical options. In Thailand, a number of sensitivity test on physical options of meteorological model had been done for small domains, mostly in coastal areas to investigate land sea breeze circulation (Phan and Manomaiphiboon, 2012) or to assess wind energy resources (Manomaiphiboon, 2009), or to prepare meteorological input for air quality modeling in an polluted area of interest (Industrial Eastate Authority of Thailand-IEAT, 2004). However, there is no sensitivity assessment for regional domain which is useful for regional modeling application.

This study aims to investigate and provide a sensitivity analysis of the physical configuration of the MM5 application in Thailand. Expected results are to figure out best physical options for each of four episodes which is representative for each season in Thailand. Outcome of this work is useful to provide options for air quality modelers for each of 5 regions during each of 4 seasons in Thailand. In particular, if deposition is a focus, choice of physical options results fair to good precipitation should be chosen while if concentration of photochemical related species is a focus, fair to good results on temperature and radiation are required.

4.2.3.2. Parameterization of the Experiments

To investigate physical option for MM5 model that is suitable for the purpose of investigating Hg concentration and deposition in Thailand, physical options from meteorological of similar study has been reviewed and summary of sensitivity test options is listed in Table 4.3 below.

Table 4.3: Sensitivity Test Options Used in the Experiments

Case ID.	**MM5 Physical Option**					**Ref.**
	Cumulus Parameterization	**PBL Scheme**	**Explicit Moisture Scheme**	**Radiation Scheme & Diffusion**	**Surface Scheme**	
1	Grell	MRF	Simple ice	Cloud radiation scheme	Five layer soil model	MM5 test case (PSU/NCAR, 2005) and adopted from (Manomaiphiboon, 2009)[a]
2	Grell	ETA	Simple ice	Rapid Radiative Transfer Model (RRTM)	Noah	(Environ International Corporation, 2009)
3	Kain-Fritsch 2	ETA	Simple ice	RRTM	Noah	(Phan and Manomaiphiboon, 2012)

a) Original physical option is Blackadar (as PBL Scheme), multi-layer soil model (as land-surface model), and Grell. The sensitivity used MRF instead of Blackadar following the application of an investigation of ozone using MM5-CAMx in Vietnam (Tran, 2008)

4.2.3.3. Selection of Episodes

Simulations were performed to prepare meteorological input for investigating the seasonal variation of Hg deposition. Therefore, episode should reflect the seasonal variation of weather change. According to TMD climatologically diagram in year 2010 as shown in Figure 4.3, four episodes were chosen, i.e., February, May, August and November in year 2010, each last one full month with 10 day spinning up.

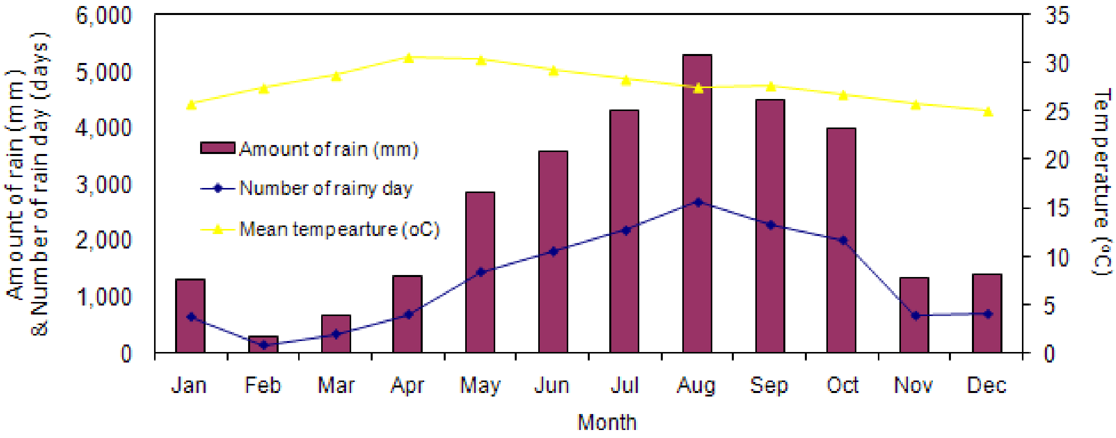


Figure 4.3: Climatological Data of Thailand Year 2010

4.2.3.4. Validation of the Outputs from Conducted Experiments

a) Data Available for Validation

Among 54 meteorological observation station at ground level belonging to TMD, 5 airport stations located in and representative of different regions of Thailand were chosen, i.e. Chiangmai, Khonkaen, Suwanabhumi, Phuket, and Hatyai. Available meteorological parameters include wind speed, wind direction, temperature, relative humidity, precipitation and solar radiation. Wind parameters were monitored at 10 m while other parameters such as temperature, humidity were monitored at 2 m. Example of meteorological data was shown in Appendix B. Information on station location is described in Table 4.5 below.

Table 4.4: List of TMD Meteorological Station Used in This Work

a) Ground Airport Station

Name	Station ID[a]	Region	Latitude	Longitude	I	J
Chiangmai	327501	Northern	18.771	98.972	137	58
Khonkaen	381201	Northeastern	16.462	102.786	116	91
Suwannabhumi		Central	13.667	100.75	91	73
Phuket	564202	Southern	8.133	98.317	40	52
Hatyai	568502	Southern	6.917	100.433	29	71

a) Station ID following Thai Meteorological Department

Table 4.4: List of TMD Meteorological Station Used in This Work

b) Sounding Station

Name	Station ID[a]	Region	Latitude	Longitude
Chiangmai	327501	Northern	18.47	98.59
Bangkok Metropolitan	455201	Central	13.44	100.30
Phuket	564202	Southern	8. 8	95.19
Songkhla	568501	Southern	7.11	100.37

a) Station ID following Thai Meteorological Department

b) Approaches

Table 4.4 below presents the statistical functions used in the statistical evaluation of meteorological models adapted from (Emery *et al.*, 2001). The analysis tool, namely "Readv3_time_series" from UCAR (ftp://ftp.ucar.edu/mesouser/MM5V3/Util), was adapted to extracted information from modeling for paring comparison with observation data.

Table 4.5: Evaluation Statistical Function (Emery *et al.*, 2001)

Parameters	**Formula**
Mean bias (MB)	$MB = \frac{1}{N}\sum_{i=1}^{N}(O_i - M_i)$
Mean absolute gross error (MAGE)	$MAGE = \frac{1}{N}\sum_{i=1}^{N}\lvert O_i - M_i\rvert$
Root mean squared error (RMSE)	$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(O_i - M_i)^2}$
Index of Agreement (IOA)	$1 - \left[\frac{N \times RMSE^2}{\sum_{i=1}^{N}\left(\lvert\overline{O} - M_i\rvert + \lvert O_i - \overline{O}\rvert\right)^2}\right]$

M: modeled value (obtained from model outputs); O: observations; $\overline{O}$: mean observation; N: number of observations

4.3. Results and Discussions

4.3.1. Results of Sensitivity Test and Scheme Selection

4.3.1.1. Results of Sensitivity Test

In Table 4.6 below, the quantitative evaluation of different simulation option is presented (and details of comparison are shown in Appendix B). The details of statistical evaluation with 3 hourly data from the Thai Meteorological Department are shown in Table 4.6. It should be noted that simulations in this work was performed for 4 full months i.e., February, May, August and November with regional scale, therefore, it is rarely or impossible to have one physical options fit all the season and location.

Temperature

On average, the MB of temperature is 1.97 to 2.64 with station MB ranging from -0.13 to 5.03. As seen in Table 4.6, station near the coastal areas (i.e., HY and PK) seems to have better agreement with observation compared to those in near the urban (i.e., SW) and mountain (i.e., CM and KM) areas. In particular, first option (Combination of Grell, MRF,Cloud raditation scheme, five layer model soil) provide good agreement for rainy season for all station with MB=0.16, especially in SW with MB=0.27 in Aug. Rainy season has good agreement for temperature for all station and all options, which best agreement was found with option 1, fair agreement in option 3 and worse in option 2. For all season, Station PK has best agreement among other station, which highest agreement was found in option 3 MB=-0.13 (which is defined as coastal option in this work). Option 3 provides good agreement for coastal areas (i.e., PK and HY), and option 1 provide better agreement for mountainous and hilly areas as compared to option 2 and 3. All case has high Index of Agreement IOA, which more than 0.9 for all the case. Temperature is underestimated, one of possible reason is out of date of land use which is not capture the urbanization which has urban heat, and this effect can be seen in SW, CM and KK areas.

Wind speed

In comparison with wind speed at 10 m from the TMD observations, it can be seen that wind speed is in good agreement with the observation in average (MB = (-0.67) – (0.47), MAGE= (2.73) – (3.21), and RSME= (0.21) – (0.25). It is underestimated in Feb and slightly overestimated for other seasons, excepted that it is always underestimated in SW station. Among option, option 1 provides better agreement compared to option 2 and 3.

Wind direction

In comparison with wind direction at 10 m from the TMD observations, it can be seen that wind direction is generally not in good agreement with observation. It is possible that different land uses and surface roughness causes different turbulence and wind direction.

Precipitation

Monthly accumulated precipitation is presented in Figure 4.4. The simulation reflects seasonal variations (i.e. distinguishing characteristics of dry season with low precipitation in February and November and wet season with high precipitation in May and August). Among the 3 cases, cases 2 and 3 provides over estimates for almost all the month (except February).

Table 4.6: Statistical Evaluation of MM5 Sensitivity Test by Station

a) Temperature at 2 meters

Statistical Function **Station**	**MB**			**MAGE**			**RSME**			**IOA**		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
CM	3.33	4.51	5.03	3.85	4.83	5.19	0.29	0.35	0.37	0.98	0.98	0.97
KK	3.02	2.92	3.69	3.38	3.36	3.98	0.26	0.25	0.29	0.99	0.99	0.98
SW	2.27	3.41	3.61	2.85	3.67	3.94	0.21	0.27	0.29	0.99	0.98	0.98
HY	0.68	1.89	0.99	1.75	2.25	1.65	0.14	0.18	0.13	0.99	0.99	1.00
PK	0.55	0.48	-0.13	1.99	2.04	1.96	0.16	0.17	0.16	0.99	0.99	0.99
Average (this study) [a]	1.97	2.64	2.64	2.76	3.23	3.34	0.21	0.25	0.25	0.99	0.99	0.98
(Emery *et al.*, 2001) [b]	< ±0.5			< 2						≥ 0. 6		
(Zhang *et al.*, 2011) [c]	(-0.3) – (-0.4)						2.8 – 3.1					

Table 4.6: Statistical Evaluation of MM5 Sensitivity Test by Station

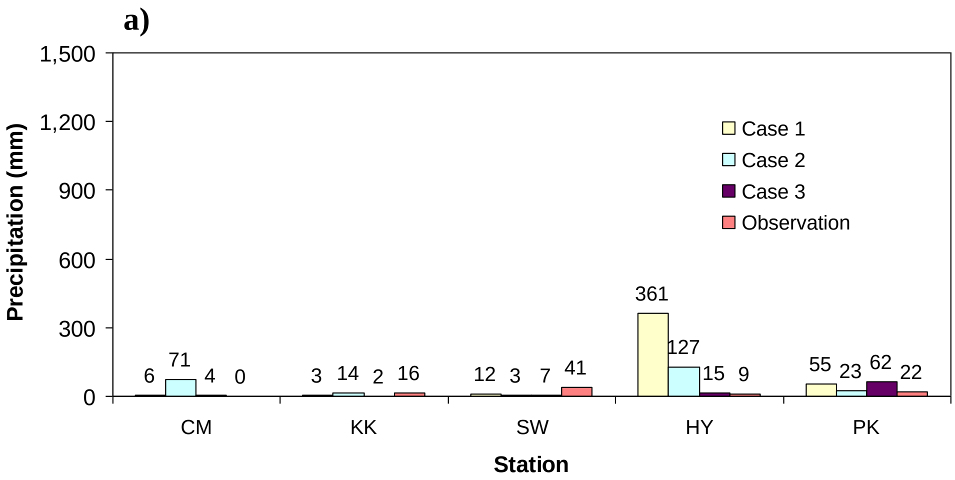
b) Wind Speed at 10 meters

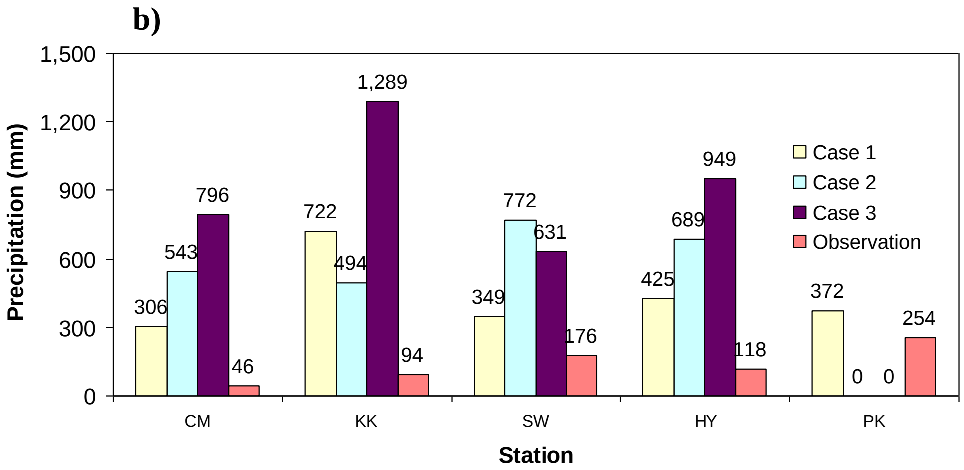
Statistical Function	**MB**			**MAGE**			**RSME**		
Station	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
CM	0.04	-0.33	-0.98	2.82	2.99	3.34	0.21	0.22	0.25
KK	-0.96	-1.37	-2.31	3.28	3.58	4.12	0.25	0.27	0.31
SW	2.90	3.11	2.41	3.31	3.67	3.62	0.26	0.29	0.29
HY	-0.17	-1.50	-1.74	2.00	2.35	2.55	0.16	0.18	0.19
PK	0.53	-0.67	-0.71	2.23	2.53	2.43	0.18	0.20	0.20
Average (this study) [a]	0.47	-0.15	-0.67	2.73	3.02	3.21	0.21	0.24	0.25
(Emery *et al.*, 2001) [b]							< 2		
(Zhang *et al.*, 2011) [c]	1.4 – 1.8						2.6 – 3.0		

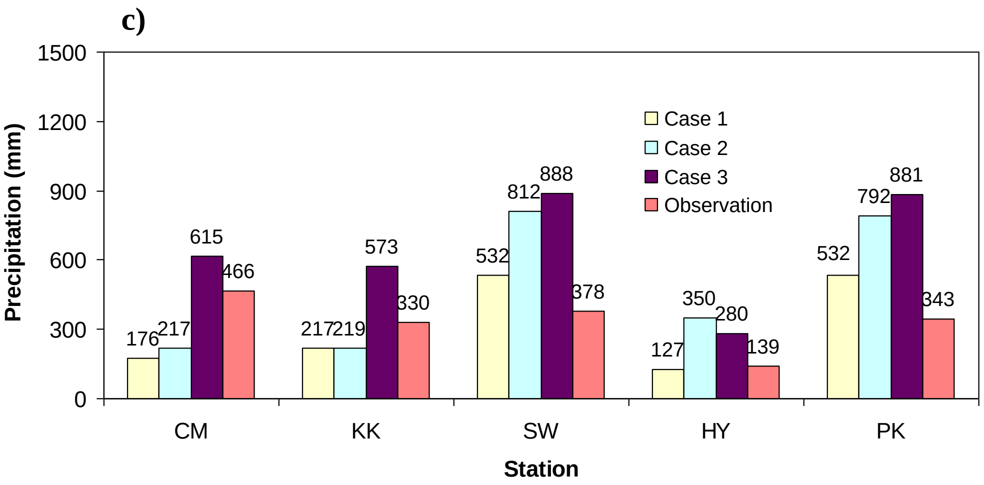
Table 4.6: Statistical Evaluation of MM5 Sensitivity Test by Station

c) Wind Direction at 10 meters

Statistical Function **Station**	**MB**			**MAGE**			**RSME**		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
CM	-113.94	-134.52	-198.31	154.74	173.53	198.40	11.80	13.58	14.64
KK	-81.81	-76.15	-138.21	124.67	124.85	138.33	9.86	10.23	10.73
SW	-1.06	-7.67	-162.15	56.76	95.38	162.47	5.15	7.88	12.29
HY	-58.86	-88.96	-167.57	116.04	140.53	167.57	8.69	10.40	11.49
PK	-5.94	-1.43	-142.92	73.21	102.20	142.98	6.32	8.46	10.22
Average (this study) [a]	-52.32	-61.74	-161.83	105.08	127.30	161.95	8.36	10.11	11.87
(Emery *et al.*, 2001) [b]	< ±10			< 20					
(Zhang *et al.*, 2011) [c]	(-20.9) – (-80.9)								


a)
Precipitation (mm)
1,500
1,200
900
600
300
0
Case 1
Case 2
Case 3
Observation
6
71
4
0
3
14
2
16
12
3
7
41
361
127
15
9
55
23
62
22
CM
KK
SW
HY
PK
Station


b)
Precipitation (mm)
1,500
1,200
900
600
300
0
1,289
796
543
306
46
722
494
94
772
631
349
176
949
689
425
118
372
0
0
254
Case 1
Case 2
Case 3
Observation
CM
KK
SW
HY
PK
Station


c)
Precipitation (mm)
1500
1200
900
600
300
0
Case 1
Case 2
Case 3
Observation
176
217
615
466
217
219
573
330
532
812
888
378
127
350
280
139
532
792
881
343
CM
KK
SW
HY
PK
Station

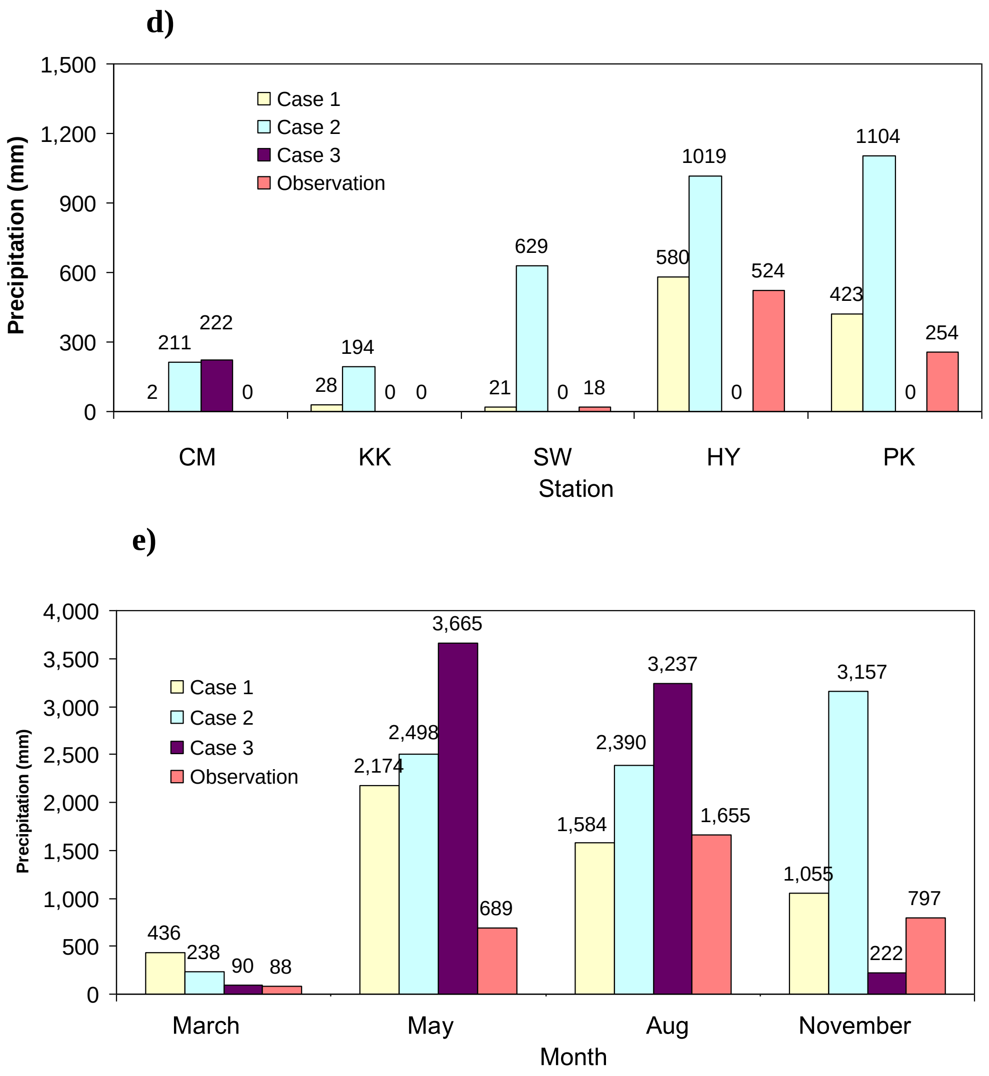


Figure 4.4: Comparisons of Observed and Simulated Precipitation by Station for a) March, b) May, c) August, d) November and e) Combined.

Table 4.7: Country Average of Statistical Evaluation of MM5 Sensitivity Test

Statistical Function	**MB**			**MAGE**			**RSME**			**IOA**		
Parameter	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Temperature	1.97	2.64	2.64	2.76	3.23	3.34	0.21	0.25	0.25	0.99	0.99	0.98
Wind speed	0.47	-0.15	-0.67	-0.67	3.02	3.21	0.21	0.24	0.25	0.99	0.98	0.98
Wind direction	-52.32	-61.74	-161.83	-161.83	127.30	161.95	8.36	10.11	11.87	0.41	0.29	0.27
Precipitation	-53%	93%	67%									

4.3.1.2. Scheme Selection

Differences between the observation and the simulation of MM5 could arise from the reasons below:

- Model resolution is relatively crude (i.e., 36 km and 12 km) and the results from a grid is an average value extracted to compare with observation which is reprehensive for single location (i.e., monitoring station)
- One set of combined physical options are fit best for some specific terrains (such as mountain, valley, coastal or urban areas) in a particular type of weather (i.e. dry season or wet season); therefore, it is no options can results best for large domain and for several seasonal runs.
- In general, scheme 1 (with combination of Grell, MRF, Simple ice, Cloud radiation scheme, and Five layer soil model) is the best match to the pattern of observed data. Based on the overall performance evaluation of MM5, the result simulated by using scheme No.1 was selected to run with the CAMx model.

4.3.2. Seasonal Variation Results of Selected Scheme

The time series of the observation and the simulation is presented in Appendix B. In this section, seasonal variation of meteorological parameter for entire domain is presented and discussed.

4.3.2.1. Temperature

In Thailand, March to May is the warmest month of the year and the average temperature is from 21-30 ^{o}C. Among the regions, the temperature in the Southern region is mild throughout the year due to the influence of sea breezes, while in the upper regions, temperature can change significantly (i.e. it can be cold in the winter and hot in the summer).

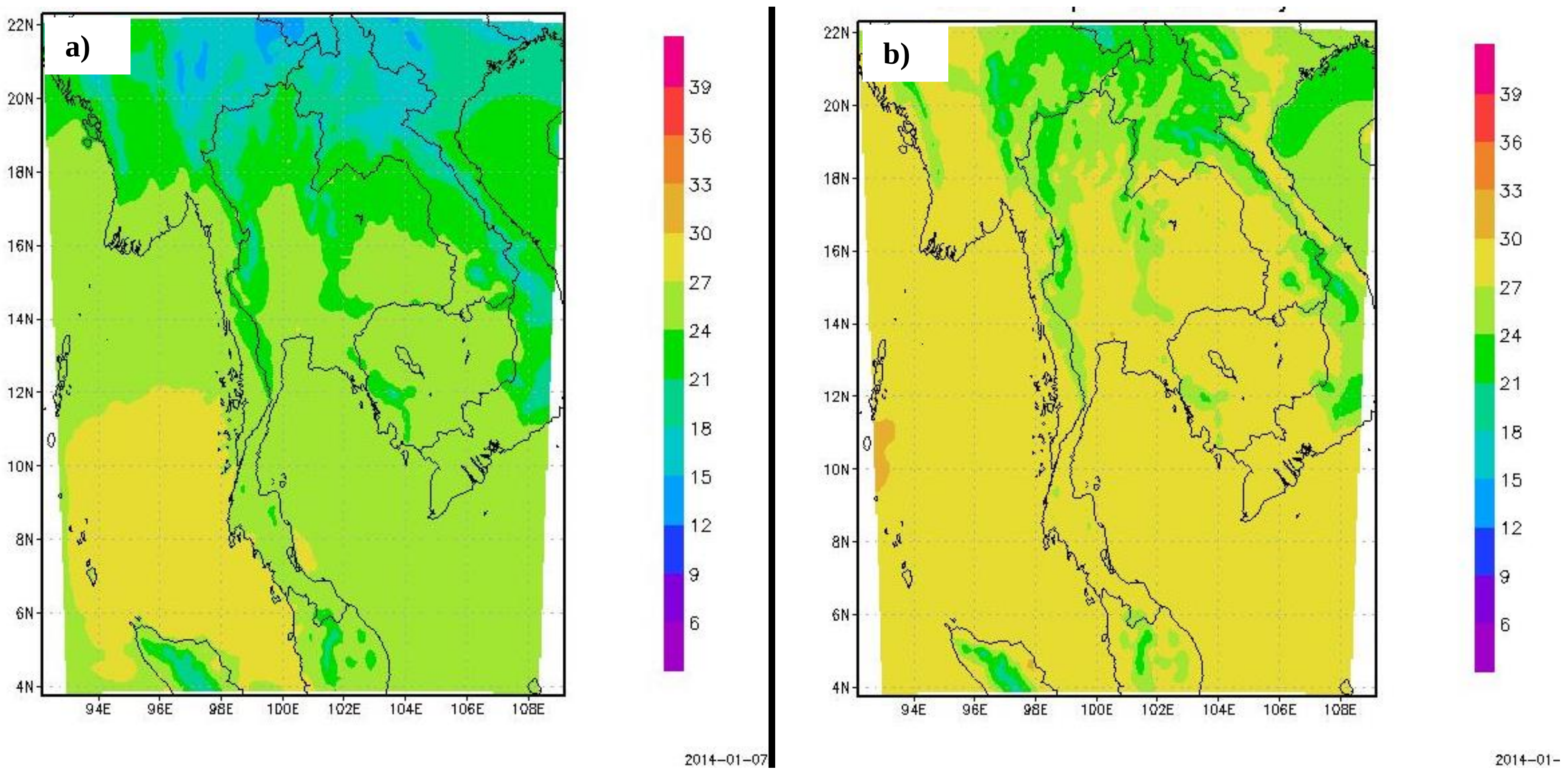


Figure 4.5: Monthly Average Temperature at 2 m over Entire Domain in a) March, b) May, c) August, and d) November

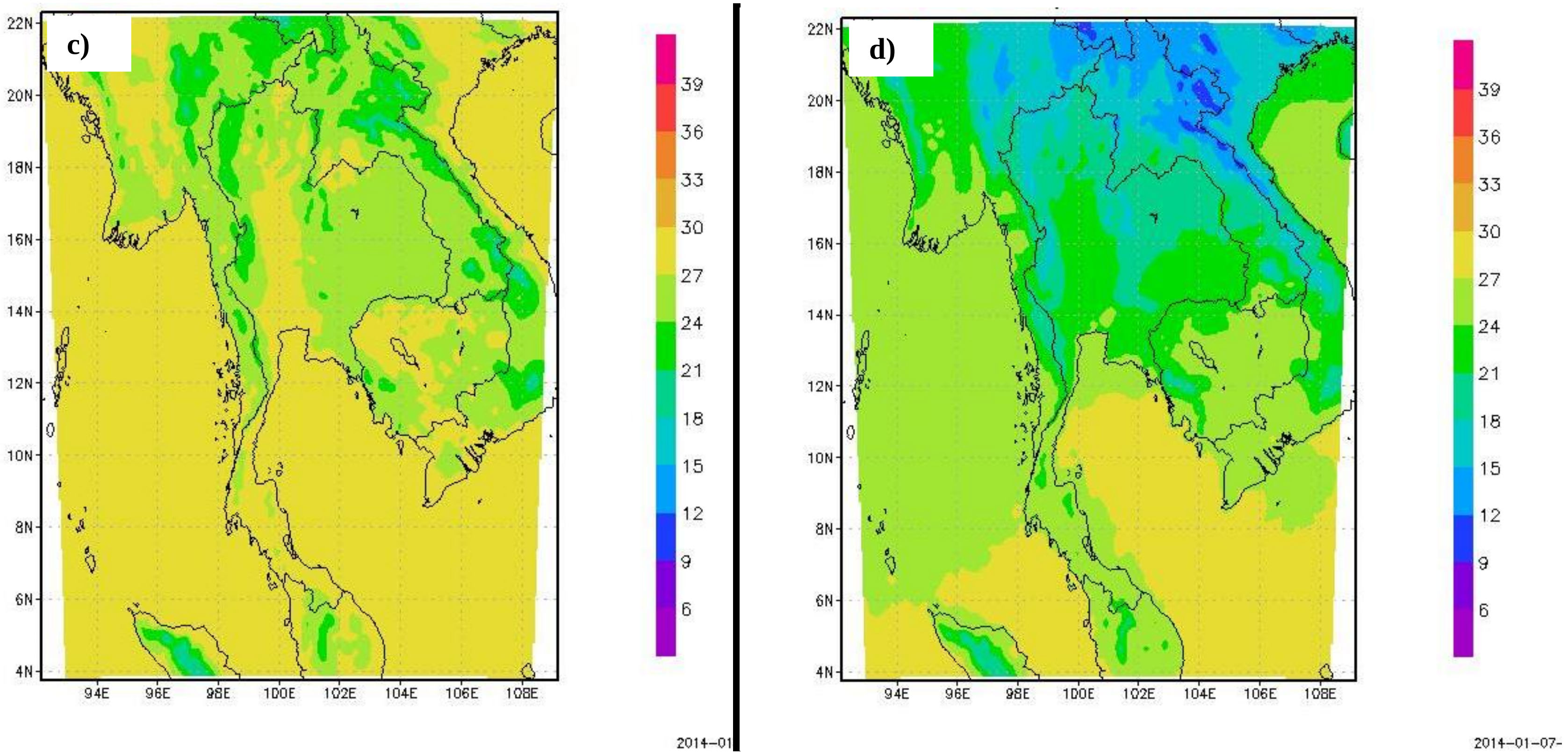


Figure 4.5: Monthly Average Temperature at 2 m over Entire Domain in a) March, b) May, c) August, and d) November

4.3.2.2. Relative Humidity

Relative humidity in Thailand ranges from 60 to 80, which is less during the summer, medium during the winter, and relatively high during the rainy season.

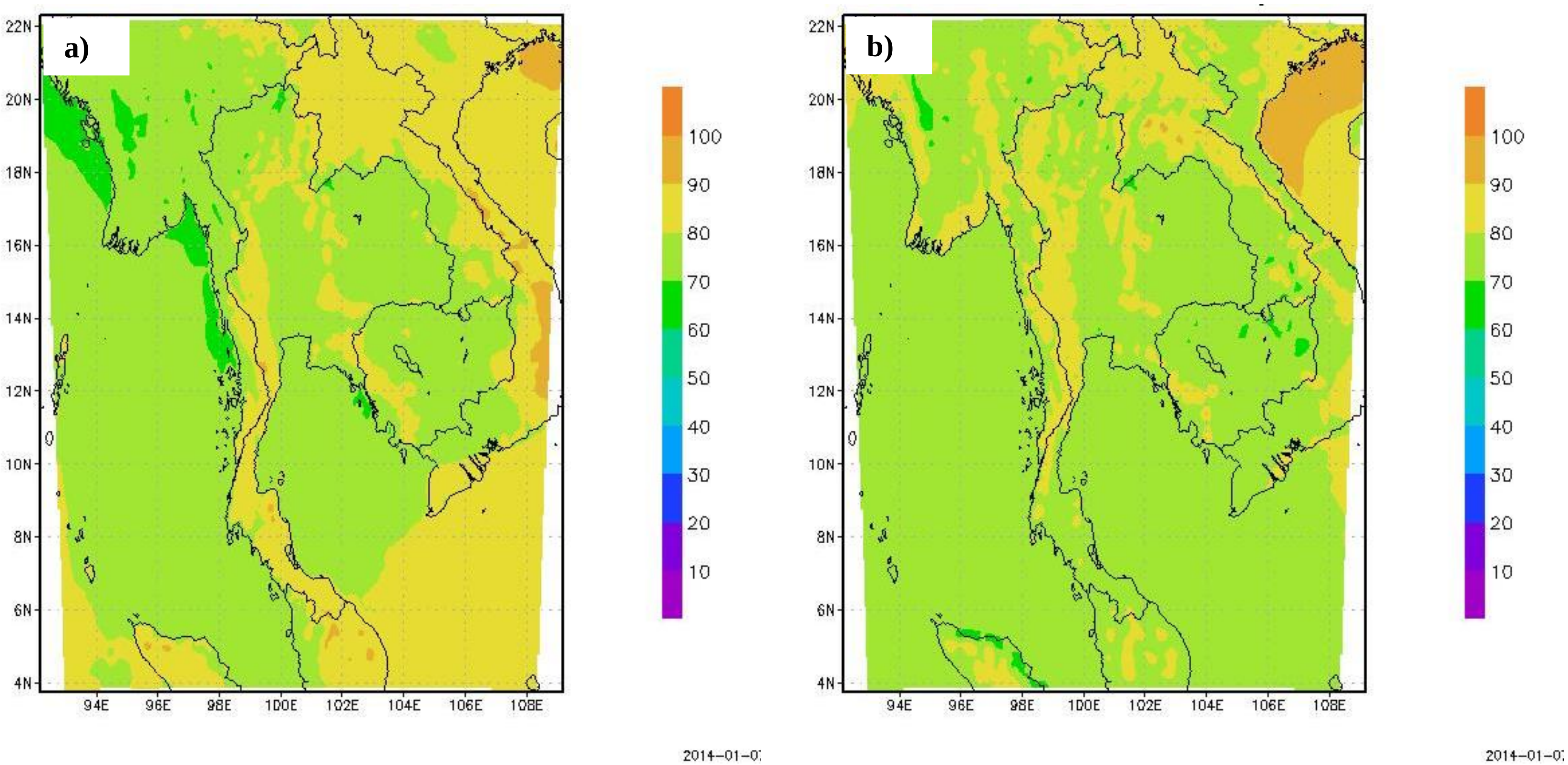


Figure 4.6: Monthly Average Relative Humidity at 10 m over Entire Domain in a) March, b) May, c) August, and d) November

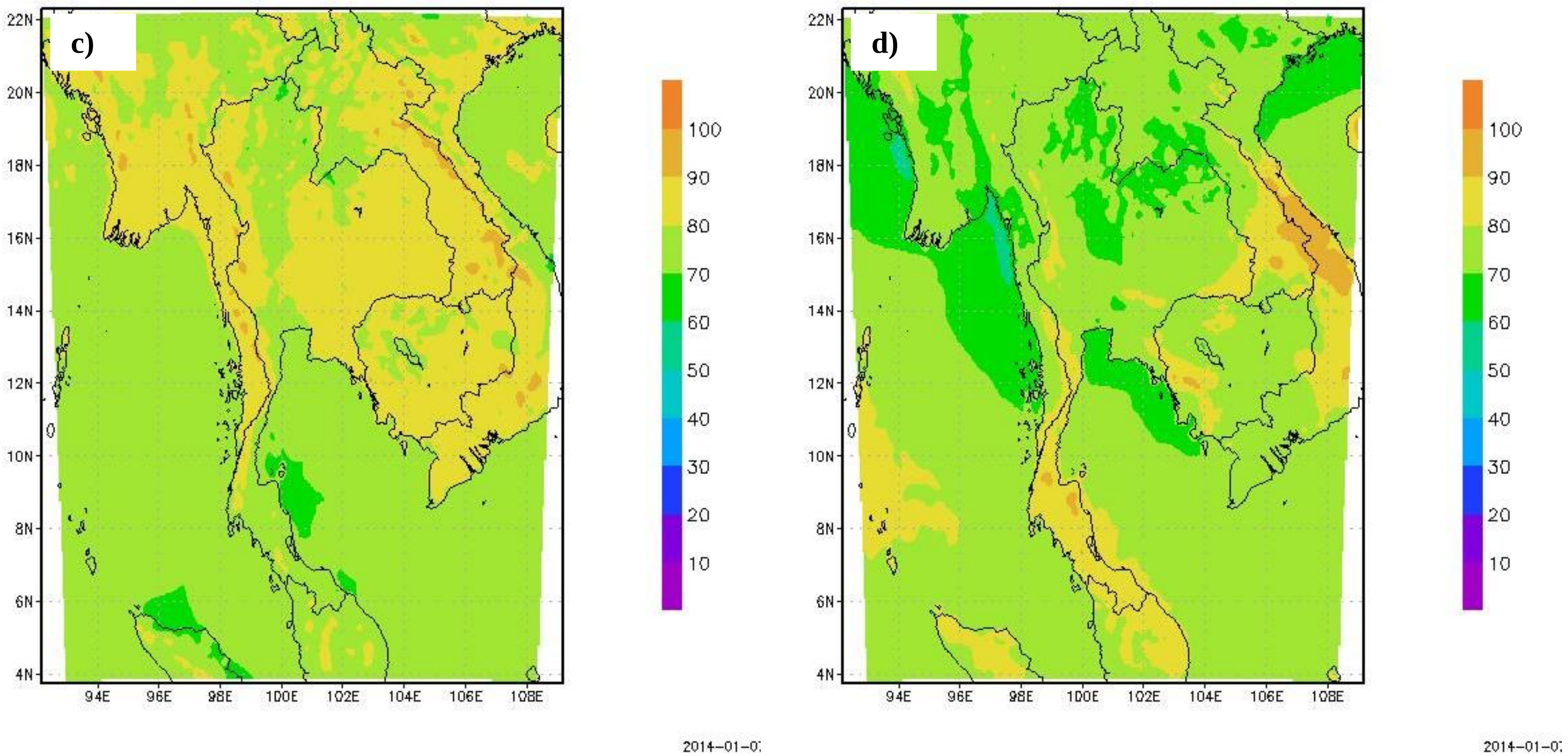


Figure 4.6: Monthly Average Relative Humidity at 10m over Entire Domain in a) March, b) May, c) August, and d) November

4.3.2.3. Wind Speed and Wind Direction

Wind characteristics in Thailand are influenced by the monsoon system. Prevailing winds during the northeast monsoon season are mostly in the north and the northeast in upper Thailand and the east or the northeast in the Southern part. During southwest monsoon: south, southwest and west over the country. In summer, prevailing wind are mostly in the south, especially in upper Thailand. A cyclone in Thailand started from April each year and strong in November in the Southern region. The model also captured this characteristic.

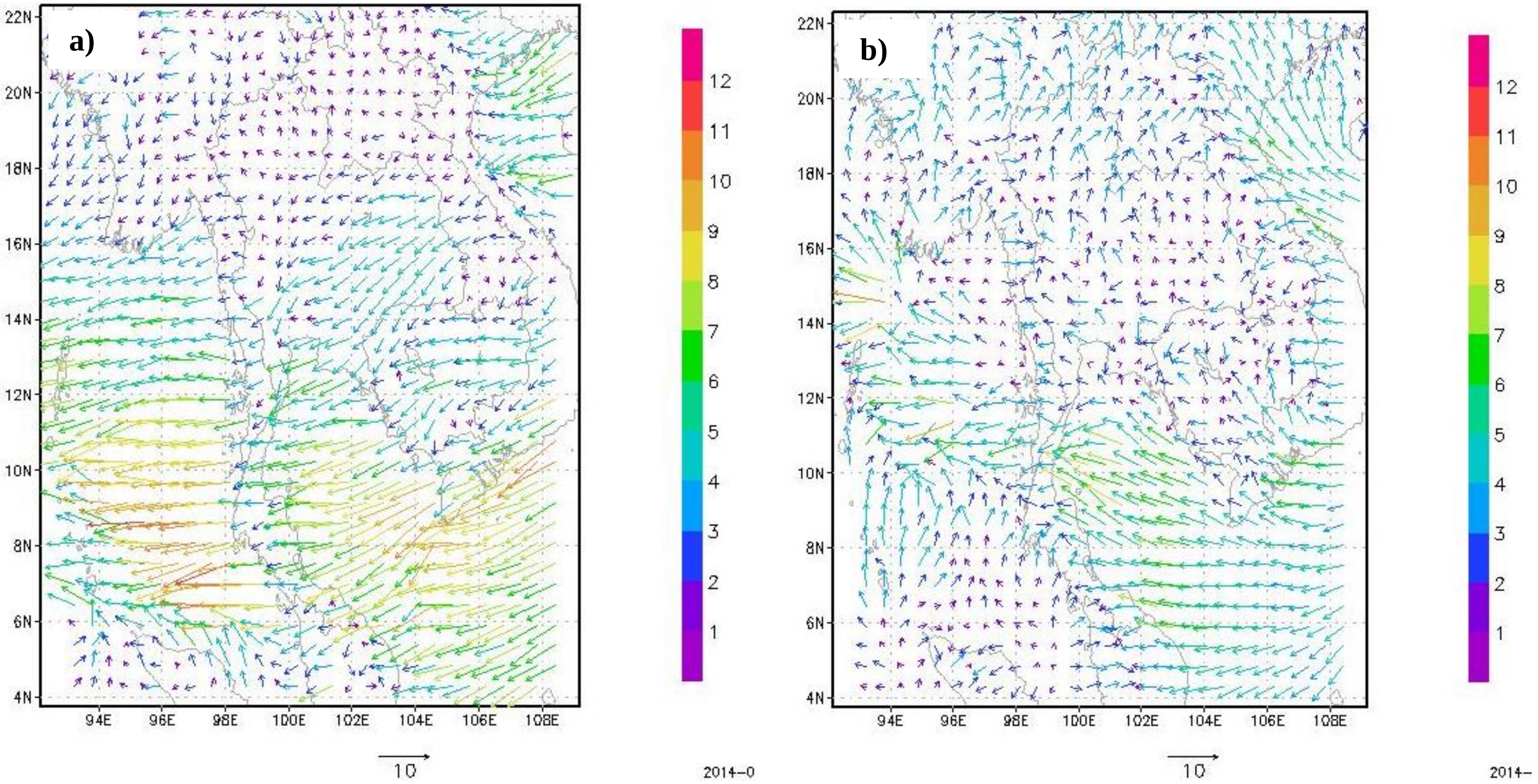


Figure 4.7: Typical Wind Vector over Entire Domain in a) March, b) May, c) August, and d) November

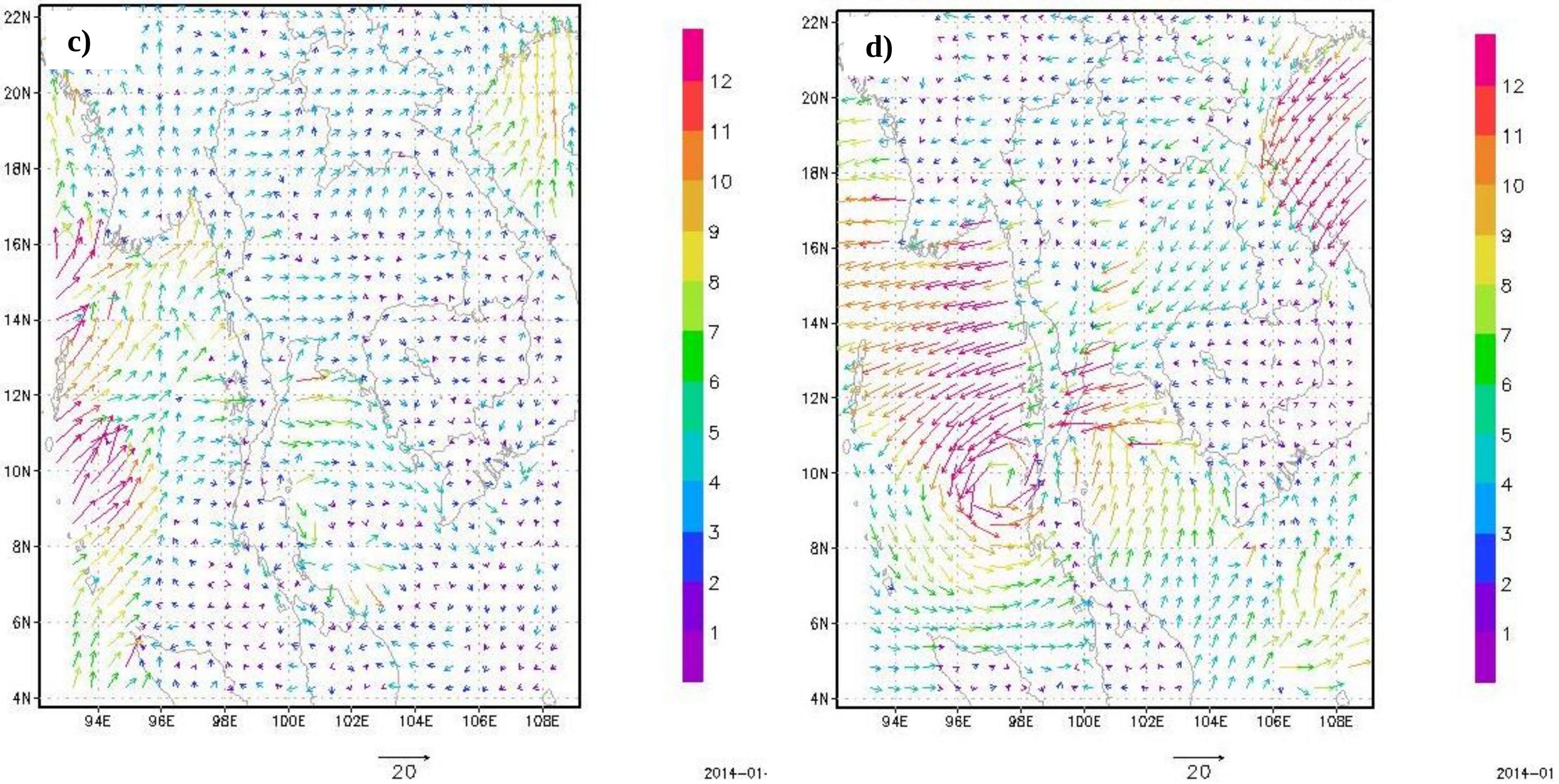


Figure 4.7: Typical Wind Vector over Entire Domain in a) March, b) May, c) August, and d) November

4.3.2.4. Precipitation

During the first half of the year, the upper part of Thailand is influenced by the northeast monsoon, therefore, this region experience dry weather. From May to October, this is season of intensive rainfall and rainfall is peak in August or September.

Unlike the upper part, the southern part of Thailand has abundant rains throughout the whole year during both the southwest and the northeast monsoon period. The rainfall peaks during August or September. During the southwest monsoon, rainfall in the west coast is peak in August or September and rainfall in the east coast is peak in November.

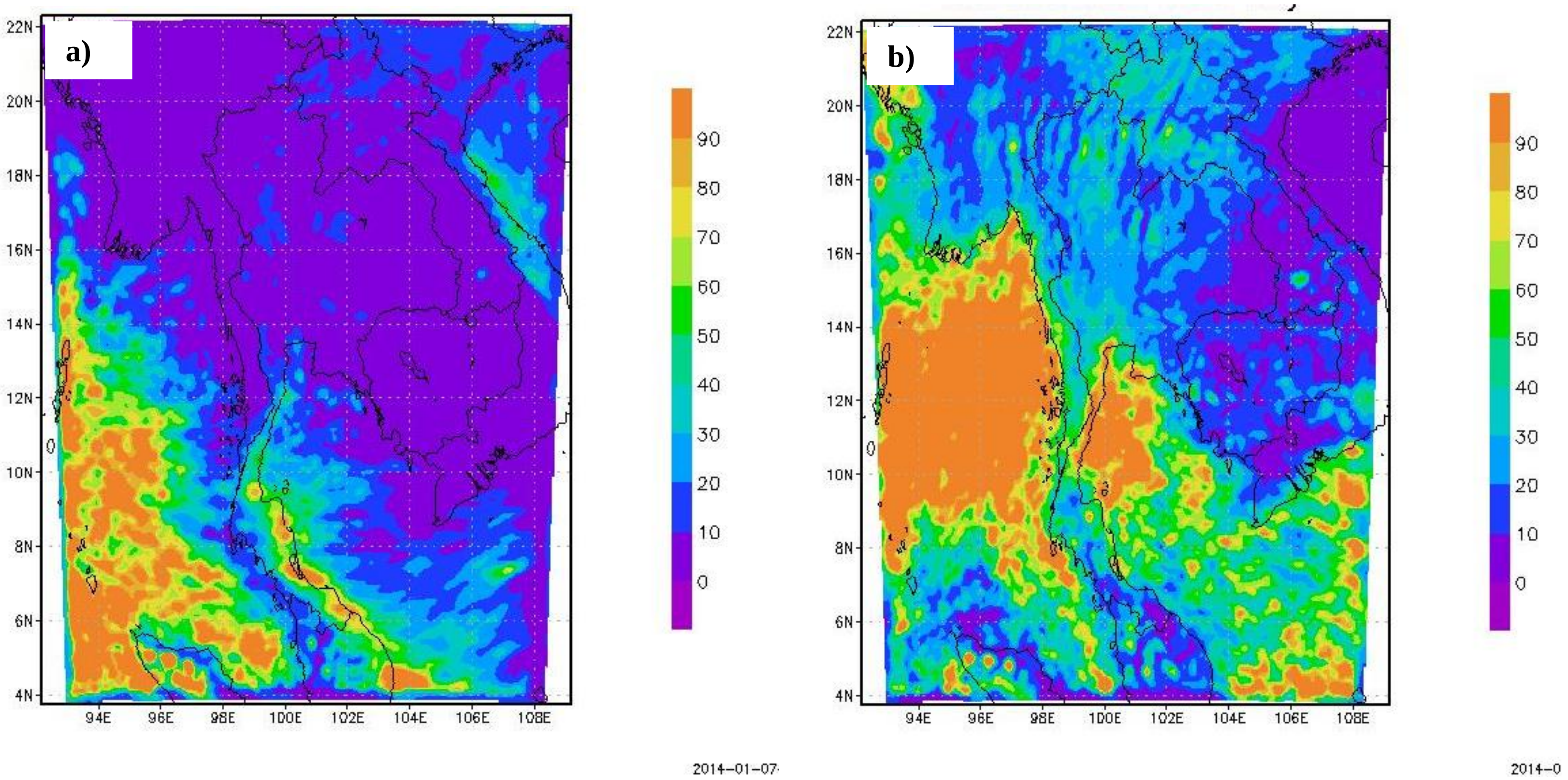


Figure 4.8: Monthly Accumulated Precipitation over Entire Domain in a) March, b) May, c) August, and d) November

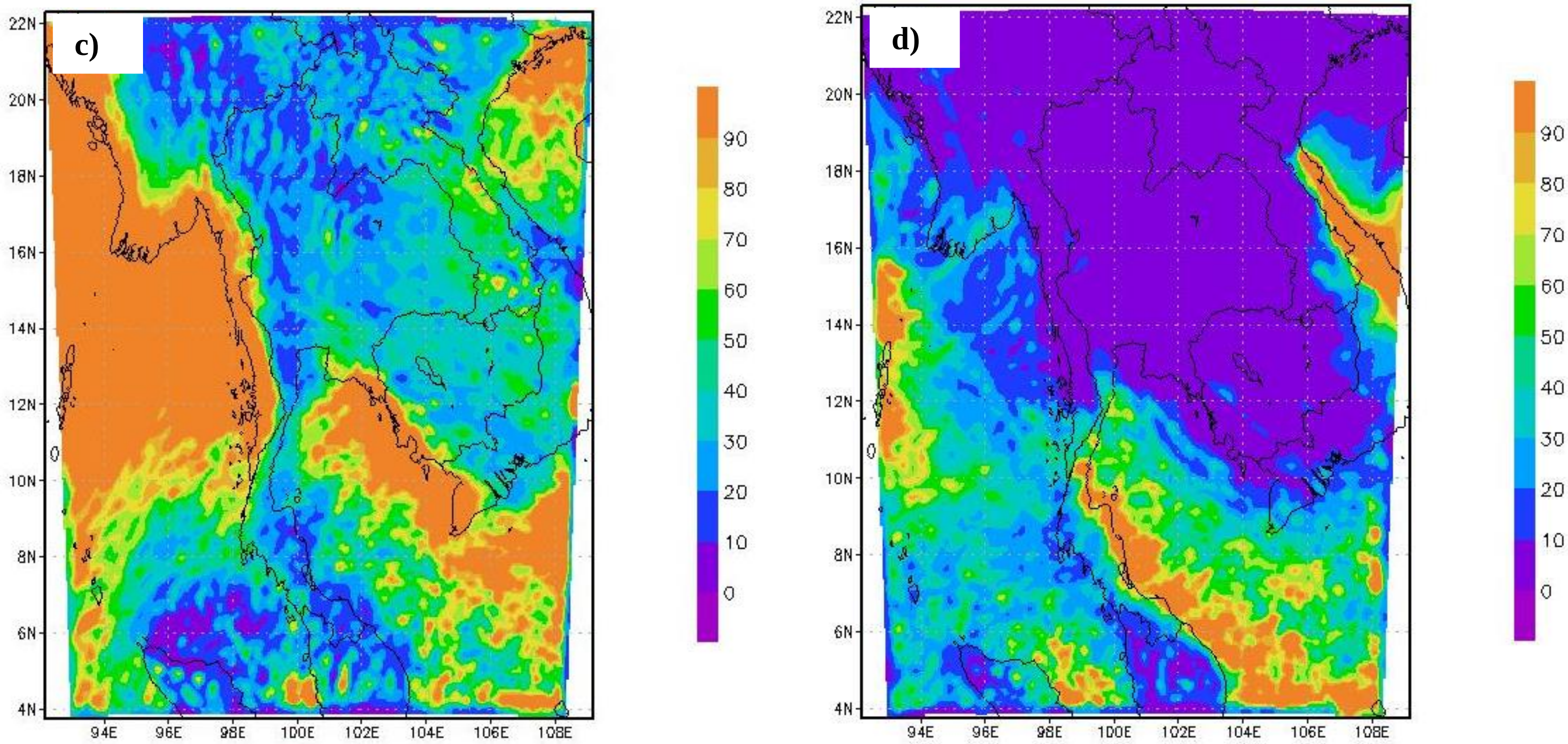


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Figure 4.8: Monthly Accumulated Precipitation over Entire Domain in a) March, b) May, c) August, and d) November

4.4. Chapter Summary

As one of the key inputs for air quality modeling, the robustness of meteorological outputs is crucial in assessing the fate of emissions. Meteorological parameters such as wind speed, wind direction, temperature, and radiation highly contribute to uncertainties of air quality model. These uncertainties can be much reduced if the applications choose appropriate physical options. This chapter has analyzed meteorological condition in Thailand to choose episode that representative for investigate seasonal variation of Hg deposition. It is 3 physical combined options were chosen for sensitivity test. In general, all options capture the temporal variation of meteorological parameters in Thailand which influence by monsoon. The comparison with 3 hourly data with Thai Meteorological Department, temperature at 2m is underestimated up to 2^{o}C and wind speed is overestimated and wind direction is high uncertainties. It is found that there is no combined options are best throughout Thailand for all year long. Among the 3 investigated physical options, the combination of Grell, MRF, Simple ice, Cloud radiation scheme, and the Five layer soil model are in better agreement with the observation than are the other options. Meteorological output of this option is used to further process for use as input for air quality model. Limitation and recommendation for future work: for future work, simulation of all months in the year should be performed and included in statistical evaluation for all available stations. Land use should be updated to the current year to better reflect better realistic situation on simulation.

CHAPTER 5
AIR QUALITY MODEL

5.1. Description of CAMx

5.1.1. Principle of CAMx

The Comprehensive Air Quality Model with extension (CAMx) is an Eulerian photochemical dispersion model with the concept of “one atmosphere” that includes the assessment of all possible tropospheric air pollution, such as O3, PM, toxic and Hg. The model has capacity for regional to continental domain. It is Fortran-code and open source. Main input of CAMx include processed meteorological and processed emissions input, which are needed to prepared separately. In Table 5.1 below, the summary of the CAMx model and the methods for key physical processes is presented.

Table 5.1: Summary of the CAMx Models and Methods for Key Physical Processes (Environ International Corporation, 2011)

Process	Physical Models	Numerical Methods
Horizontal Advection	▪ Eulerian continuity equation	▪ Bott ▪ PPM
Horizontal Diffusion	▪ K-theory 1st order closure	▪ Explicit simultaneous 2D solver
Vertical Advection	▪ Eulerian continuity equation	▪ Implicit backward Euler (time) hybrid centered/upstream (space) solver
Vertical Diffusion	▪ K-theory 1st order closure ▪ Non-local mixing	▪ Implicit backwards-Euler (time centered (space) solver ▪ Explicit ACM2 non-local convection/diffusion
Gas Phase Chemistry	▪ Carbon Bond 2005 ▪ Carbon Bond 2006 ▪ SAPRC 99 (Carter, 2000) ▪ Inorganic / organic aerosol percursors	▪ EBI ▪ IEH ▪ LSODE
Aerosol Chemistry	▪ Aqueous inorganic chemistry ▪ Inorganic thermodynamics/portioning ▪ Organic thermodynamics/portioning ▪ Static 2 mode or multi-section size models	▪ RADM-AQ ▪ ISORROPIA ▪ SOAP ▪ CMU
Dry Deposition	▪ Wesley Scheme for resistance model for gaseous and aerosol ▪ Zhang Scheme for resistance model for gaseous and aerosol	▪ Deposition velocity as surface boundary condition in vertical diffusion colver
Wet Deposition	▪ Scavenging model for gaseous and aerosols	▪ Exponential decay as a function of scavenging coefficient

5.1.1.1. Governing Equation

CAMx simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species (l) on a system of nested three-dimensional grids. The Eulerian continuity equation describes the time dependency of the average species concentration (C_t) within each grid cell volume on all of the physical and chemical processes operating on that volume. This equation is expressed mathematically in terrain-following height (z) coordinates

$$\frac{\partial c_i}{\partial_t} = -\nabla_H . V_H c_i + \left[\frac{\partial (c_i \eta)}{\partial z} - c_i \frac{\partial}{\partial z}\left(\frac{\partial h}{\partial t} \right) \right] + \nabla . \rho K \nabla (c_i / \rho) + \frac{\partial c_i}{\partial t}\Big|_{Chemistry} + \frac{\partial c_i}{\partial t}\Big|_{Emission} + \frac{\partial c_i}{\partial t}\Big|_{\mathrm{Re}\,moval}$$

The first three terms in the right-hand side of the equation present the pollutants transportations, which is both mass conservative and mass consistent. Chemical reaction algorithm is comprised of a set of reactions equations define by specific chemical mechanism. Pollutant removal includes both dry deposition and wet scavenging by precipitation (Environ International Corporation, 2011).

5.1.1.2. Physical Properties of the Hg Species in the Model

The physical properties of Hg species, including physical properties such as (Henry's Law, molecular diffusivity, surface reactivity) influence the concentration and the deposition characteristics. According to Henry Law, it states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid". The Hg^{2+} species represents $HgCl_2$ and $Hg(OH)_2$ in which Henry constant for the former is 1.4×10^6 M atm^{-1} and for the latter is 1.2×10^4 M atm^{-1}. The Henry constant for Hg^{2+} is assumed to be similar to that of HNO_3 because of their similar solubility. The Henry constant used for HNO_3 is 1×10^5 M atm^{-1} which is within the range between $HgCl_2$ and $Hg(OH)_2$. Normally, Henry constant of Hg^0 (set is similar to CO) is equal to 1.0×10^{-10} M atm^{-1} in the chemistry parameters file to disable dry and wet deposition of Hg^0. In this work, natural emissions of Hg^0 were included in the CAMx simulation; therefore, the Henry constant of Hg^0 was set to 0.111 (Environ International Corporation, 2011). Molecular mass of Hg species are in the following, Hg^0 with 200.59 g/mol; Hg^{2+} with 254.58 g/mol (as average of molecular mass of $HgCl_2$ and $Hg(OH)_2$).

5.1.1.3. Chemistry

This section presents the chemistry of Hg in CAMx, including gas phase, aqueous phase, and equilibrium transformation. The gas phase transformation of Hg^0 to Hg^{2+} by O_3, HCl, H_2O_2,Cl_2 and OH. In the atmospheric environment, aqueous phase reactions can occur in cloud-, fog- or rain-water and in films of moisture associated with hygroscopic aerosols. Hg related aqueous-phase chemistry involves with the reduction of Hg^{2+} to Hg^0 by using reaction with hydroperoxy radicals (HO^2) and by the formation of the sulfite complexes (at low HCl concentrations), $HgSO_3$ and $Hg(SO_3)_2^{2-}$, as well as the oxidation of Hg^0 to Hg^{2+} by dissolved O_3, OH, and Cl_2.

Table 5.2: Hg Gas Phase Reactions in CAMx (Environ International Corporation, 2011)

a) Gas Phase

Reaction	**Rate ($cm^3 molec^{-1} s^{-1}$)**
$Hg^0(g) + O_3(g) \rightarrow Hg(II)(g)$	3×10^{-20}
$Hg^0(g) + OH^\bullet(g) \rightarrow Hg(OH)_2$	8×10^{-14}
$Hg^0(g) + H_2O_2(g) \rightarrow Hg(OH)_2$	8.5×10^{-19}
$Hg^0(g) + Cl_2(g) \rightarrow HgCl_2$	26×10^{-19}
$Hg^0(g) + HCl(g) \rightarrow HgCl_2$	1×10^{-19}

Table 5.2: Hg Gas Phase Reactions in CAMx (Environ International Corporation, 2011)

b) Aqueous Phase

Reaction	**Rate** **(M^{-1} s^{-1}) unless noted**
$HgSO_3(aq) \rightarrow Hg^0(aq) + S(VI)$	0.0106 s^{-1}
$Hg^{2+}(aq) + HO_2^{\bullet}(aq) \rightarrow Hg^0(aq) + \mathrm{Pr}oducts$	1.7 x 10^4
$Hg^0(aq) + O_3(aq) \rightarrow Hg^{+2}(aq) + \mathrm{Pr}oducts$	4.7 x 10^7
$Hg^0(aq) + OH^{\bullet}(aq) \rightarrow Hg^{+2}(aq) + \mathrm{Pr}oducts$	2.0 x 10^9
$Hg^0(aq) + HOCl(aq) \rightarrow Hg^{+2}(aq) + Cl^{\bullet} + OH^{\bullet}$	2.09 x 10^6
$Hg^0(aq) + OCl^{\bullet}(aq) \rightarrow Hg^{+2}(aq) + Cl^{\bullet} + OH^{\bullet}$	1.99 x 10^6

Table 5.2: Hg Gas Phase Reactions in CAMx (Environ International Corporation, 2011)

c) Equilibrium

Reaction	**Rate**
$Hg(0)(g) \Leftrightarrow Hg(0)(aq)$	K = 0.11 M atm^{-1}
$HgCl_2(g) \Leftrightarrow HgCl_2(aq)$	K =1.4 x 10^6 M atm^{-1}
$Hg(OH)_2(g) \Leftrightarrow Hg(OH)_2(aq)$	K =1.2 x 10^4 M atm^{-1}
$HgCl_2(aq) \Leftrightarrow Hg^{2+} + 2Cl^-$	K= 10^{-14} M^2
$Hg(OH)_2(aq) \Leftrightarrow Hg^{2+} + 2OH^-$	K= 10^{-22} M^2
$Hg^{2+} + SO_3^{2-} \Leftrightarrow HgSO_3$	K = 2.1 x 10^{13} M^{-1}
$HgSO_3 + SO_3^{2-} \Leftrightarrow Hg(SO_3)_2^{2-}$	K = 1 x 10^{10} M^{-1}
$Hg(II)(aq) \Leftrightarrow H(II)(p)$	K = 3.4 Lg^{-1}

There are some Hg species remaining in the atmosphere as Hg^P compounds, such as HgO, HgS, $HgCl_2$, $HgSO_4$, $Hg(NO_3)_2$. Possible chemical reactions related to Hg^P, including the reduction of HgO to Hg^0 by CO, SO2, NO or addition of water to form $Hg(OH)_2$.

However, due to uncertainties of Hg particulate phase and the lack of reaction rate, transformation of Hg_P is not included in current modeling effort. In CAMx, rate of chemical reaction and equilibrium in chemistry module are hard-code and thus not include in chemistry parameter input file.

5.1.2. Input Description

Adopted from CAMx User guide v5.4 (Environ International Corporation, 2011)

Table 5.3: Input Description CAMx (Environ International Corporation, 2011)

Data Types	Description
Meteorology (Supplied by a Meteorological Model)	3-Dimensional Gridded Fields: ▪ Vertical Grid Structure ▪ Horizontal Wind Components ▪ Temperature ▪ Pressure ▪ Water Vapor ▪ Vertical Diffusivity ▪ Clouds/Precipitation
Air Quality (Obtained from Measured Ambient Data)	▪ Gridded Initial Concentrations ▪ Gridded Boundary Concentrations
Emissions (Supplied by an Emissions Model)	▪ Elevated Point Sources ▪ Combined Gridded Sources ○ Low-level Point ○ Mobile ○ Area/Non-road Mobile ○ Biogenic
Geographic (Developed from Terrain and Land use /Land cover Maps, Drought Index Maps, Modeled or Satellite derived Snow Cover, Satellite-derived LAI)	Gridded Surface Characteristics ▪ Land Use Category ▪ UV Albedo ▪ Snow Cover ▪ Leaf area index (LAI) ▪ Land/Water Mask ▪ Roughness Length ▪ Drought Stress ▪ Terrain Elevation
Photolysis Derived from Satellite Measurements and Radiative Transfer Models	Atmospheric Radiative Properties ▪ Gridded Haze Opacity Codes ▪ Gridded Column Ozone Codes ▪ Photolysis Rates Lookup Table

5.1.3. Output Description

Adopted from CAMx User guide v 5.4 (Environ International Corporation, 2011)

Table 5.4: Output Description CAMx (Environ International Corporation, 2011)

File Suffix	Description
.out	Text simulation tracking file (CPU, input files read, error/warning
diag	Text simulation diagnostic file (repeat of run control inputs, PiG diagnostics, miscellaneous diagnostic output)
.mass	Text mass budget file for subsequent post-processing
.inst	Binary master grid instantaneous concentration file at the end of the simulation
.finst	Binary nested grid instantaneous concentration file at the end of the simulation (used for restarts)
.PiG	Binary PiG sub-model file (used for restarts)
.avrg.grdnn	Binary (UAM format) average concentration file for grid nn; optionally contains 2-D layer 1 concentration field or full 3-D concentration field
.depn.grdnn	Binary (UAM format) surface deposition file for grid nn
.smpnn	Binary (UAM format) average surface concentration file for PiG

5.2. Methodology

5.2.1. Air Quality Domain

Air quality domains are set to capture the effects of Hg emissions from the vicinity to Thailand. They include 2 domains: coarse and fine domains. The dimensions of coarse and fine domain of air quality model are designed as same as those of met models. The grid sizes are 36 x 36 km^2, and 12 x 12 km^2, respectively.

Table 5.5: CAMx Domain

Domain #	Map projection	Grid size (km)	Vertical level	Grid number
Domain 1	LCP[a]	36	12	131, 131
Domain 2	LCP[a]	12	12	167, 143

a) Lambert Conformal Projection

Table 5.6: Vertical Layers Used in CAMx

Height (m)	MM5 Layers	CAMx Layers
14,649	23	12
13,855	22	
12,810	21	
11,346	20	
9,058	19	11
7,277	18	
5,807	17	10
4,549	16	
3,445	15	9
2,940	14	
2,460	13	8
2,003	12	
1,568	11	7
1,152	10	
752	9	6
369	8	
183	7	5
146	6	
102	5	4
73	4	3
51	3	2
29	2	1
14	1	
Ground		

5.2.2. Work Flow & Data Preparation

Figure 5.1 presents the workflow of CAMx. In brief, emissions are processed to be CAMx ready input format and MM5 output are convert to be CAMx ready input format using

MM52CAMx program. Photolysis rates are calculated using TUV program. Boundary and initial conditions (BC/ICs) are obtained from observation and outputs of coarser modeling domain. The Carbon Bond mechanism (CB05) is applied to generate the concentrations of photochemical oxidants. GRADS program are used to visualize CAMx output.

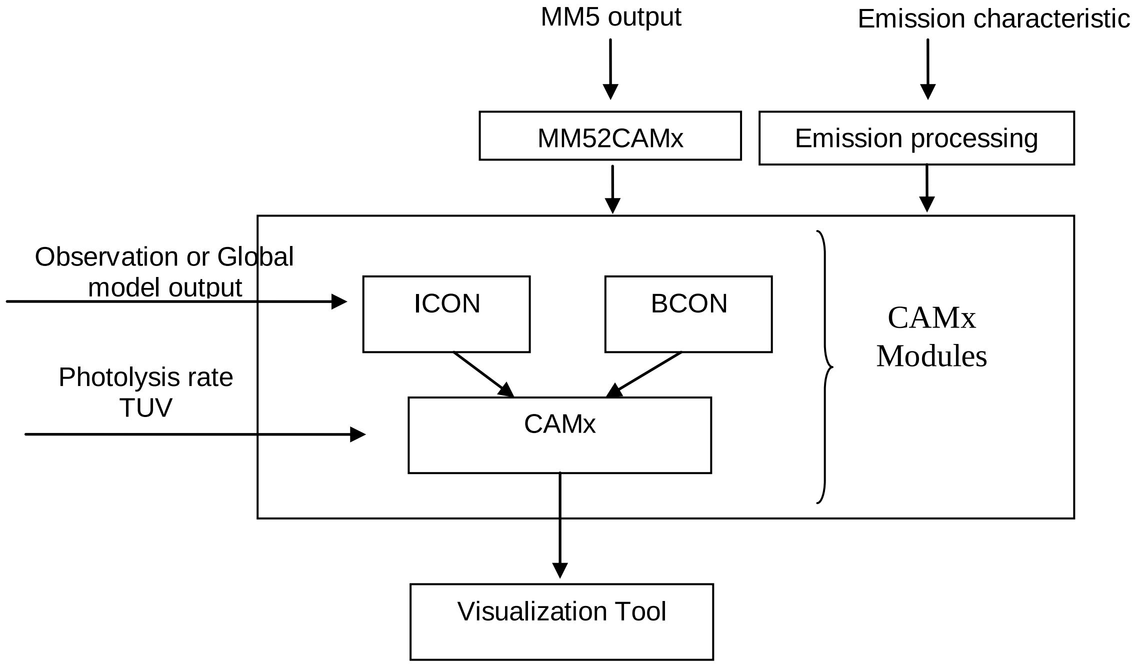


Figure 5.1: Work Flow of the CAMx Air Quality Model (Environ International Corporation, 2011)

5.2.2.1. Preparation of Emission Input for CAMx

a) Gap Fillings for Hg Species and Hg Reactants

Emissions species required for CAMx-Hg modeling are non-Hg emissions (NO_X, CO, NMVOC, SO_2, NH_3, PM_{10}, $PM_{2.5}$, OC, and BC) and Hg emissions (Hg^0, Hg^2, and Hg_P). Emission inputs are processed to have details of hourly gridded of each speciated emissions

Gridded Emissions

In this work, only Hg emissions inside Thailand have been updated with local activity data and specific EFs. However, customarily, modeling domain is rectangular which cover one or more countries of interest. In addition, emissions of other Hg reactant species such as O_3 precursor are required as model input. Wherever information of emissions are not lacking, gap fillings (normally, global or regional estimates) are used.

For the Hg species, global Hg emissions for 2010 are developed and the first draft was released to the modeling community through personal communication in early 2013 (Wilson, 2013). The dataset are in 0.5^o gridded format for 3 species (i.e., Hg^0, Hg^2 and Hg_P) for 3 vertical levels (less than 50m, 50-100m and more than 100m). Emissions of Hg reactants species (e.g., ozone precursors) for whole domain (i.e., both inside and outside Thailand) were also obtained from literature review. Among available regional database (presented in Table 2.4) that provide gridded and speciated EI, INTEX-B was chosen for the comparable in term of grid resolution with AMAP-Hg data (i.e., all of database used for gap fillings has similar grid resolution of 0.5 deg). Gridded database were downscaled to 36 km and 12 km resolution. Then the values were assigned to original 36 km or 12 km MM5 grid using nearest neighborhood technique. For QA/QC, the sum of emissions was compared before and after the downscaled processes to avoid underestimates or overestimates. INTEXT-B was projected to year 2010 using proportional scale of SEAC4RS. For emissions from biomass burning, GFEDv3 was chosen and for natural sources, GEIA was chosen. Table 5.5 below presents the emissions database used for gap fillings in this work.

Table 5.7: Emissions Database Used for Gap fillings in this Work

Dataset	**Emission Sources**	**Species**	**Temporal Coverage**	**Spatial Distribution (**(deg)	**Reference**
AMAP/ UNEP	Global Anthropogenic	Hg^0, Hg^2, Hg_P	2010	0.5	On request (personal communication with Mr. Frits Steenhuisen, Arctic Centre, University of Groningen, the Netherlands)
INTEX-B	Asia Anthropogenic[a]	NO_X, SO_2, CO, NMVOC, NH_3, PM_{10}, $PM_{2.5}$, OC, BC	2010 (projected from year 2006)[b]	0.5	http://cgrer.uiowa.edu/projects/emmison-data (Assessed by Nov 11, 2013)
GFED.v3	Global Biomass Burning	NO_X, SO_2, CO, NMVOC, NH_3, $PM1_0$, $PM_{2.5}$, OC, BC	2010	0.5	http://globalfiredata.org/ (Assessed by Nov 11, 2013)

a) Gridded emissions presented by sector (e.g., power plant, industry, mobile, agriculture)

b) Anthropogenic emissions from INTEX-B for year 2006 were projected to year 2010 using projected factor from SEAC4RS (http://www.cgrer.uiowa.edu/SEAC4RS/emission.html). That is $E_{INTEX\text{-}B}$ (species i) year 2010 = $E_{INTEX\text{-}B}$ (species i) year 2006 x ratio ($E_{SEAC4RS}$ (species i) year 2010 / $E_{SEAC4RS}$ (species i) year 2006).

Vertical Distribution of Emissions

Emissions datasets employed for the air quality model were obtained from different sources (as mentioned in Table 5.5). Emissions presented in different format in terms of spatial and vertical resolutions. While emissions from natural sources and biomass burning can be considered as areas sources (i.e., emitted at ground or near ground layers), emissions due to combustion process from large stationary point sources (i.e., large power plant and large industrial facilities (under anthropogenic sources) can be treated as elevated point emissions. Existing database of anthropogenic emissions for this work (i.e., INTEX-B and AMAP/UNEP) do not provide exact details that sufficient for process emissions to elevated point sources (i.e., location of stack, stack height, stack diameter and flow rate). Emissions in this study were treated as area sources. That means that all emissions have been assumed to release in the first layer of air quality model, which is approximately 30m.

Emissions Speciation

According to the literature review, the emissions species required for Hg chemistry include species involved in the photochemistry, such as NMVOC speciation, and PM speciation. Carbon Bond mechanism has been employed in study on Hg concentration and deposition (Yarwood *et al.*, 2003; Lin *et al.*, 2006). Regional emissions obtained from existing regional database provide emissions as grouped species and modeler need to seek for appropriate speciation profiles to convert that grouped emissions to speciated emissions ready for modeling input. Emissions development often also suggested guidance for emissions speciation. For example, mapping table to convert NMVOC and PM speciation to CB4 following profiles during TRACE-P campaign (Fu *et al.*, 2004) has been developed and presented speciation for combined anthropogenic sources. The profiles have been used in many applications for regional air quality models. Example for application in Southeast Asia is the study on hindcasting and forecasting O3 (Le, 2008) and reasonable agreement was found between simulation and observation. Recently, during effort to harmonize emissions on a global scale for air quality modeling, a mapping table to convert NMVOC to CB5 for HTAP v2 was suggested to modeler (EDGAR, 2013). The former provides NMVOC speciation for all anthropogenic sources, while the later provides the NMVOC speciation for anthropogenic sources by sector (i.e. combustion, industrial processes, mobile etc).

Besides the regional profiles of emissions, there were some local studies on NMVOC profiles for specific domains. For example, study on O3 in Chonburi province, Thailand and development of EI for criteria gaseous and particulate species (Vongmahadlek *et al.*, 2009). The former developed NMVOC speciation profiles based on SPECIATE tools of US EPA and other local development and NMVOC speciation was presented by sources (i.e., power plant, different industrial type as well as mobile sources and biogenic sources) and the latter provide suggested one profile of NMVOC speciation for the whole country following profiles of NMVOC import/export in Thailand.

Though the emissions profiles of the NMVOC of each work are presented differently (i.e. by fuel, by process, by sector or a whole country, whole continental region) due to the method of development and application purpose, the key species for NMVOC emissions were paraffin (PAR) (accounted for 50% or more of total NMVOC emissions)

In this work, the emission speciation following the CB5 mechanism has been adopted to process INTEX-B emissions. The emissions from each speciated species (E_S) are the product of the emissions of grouped species (E_G) and the fraction of it in its corresponding group (F). According to CAMx user guide version 5.4 (Environ International Corporation, 2011), emissions for gaseous were converted to mol using its corresponding macular weight and emissions for particulate were maintained as gram. In Table 5.6 below, the chosen speciation profile of emissions following the suggestion of HTAP-EDGAR (EDGAR, 2013) and its molecular weight used in this work is presented.

Table 5.8: Speciation Profiles of Emissions Used in this Work (EDGAR, 2013)

Grouped Species (G)	**Speciated Species (S)**	**Fraction of its Corresponding Group (F)**	**Molecular Weight[a] (Unit: g/mol)**
Anthropogenic NMVOC[b]	PAR	0.562	14
	UNR	0.128	45-150
	FORM	0.122	30
	ETHA	0.048	30
	ETH	0.047	28
	OLE	0.026	27
	TOL	0.018	92
	XYL	0.012	106
	ALDX	0.011	44
	ALD2	0.011	44
	BENZENE	0.005	78
	ETOH	0.003	46
	IOLE	0.003	48
	MEOH	0.002	32
	TERP	0.001	136
	SESQ	0.000	204
	ISOP	0.000	68
	UNK	0.000	200
NO_X (as NO_2)	NO	0.900	30
	NO2	0.100	46
SO_2	SO2	0.980	64
	SULF	0.020	64
PM_{10}	PCC	0.800	
	PCS	0.200	
$PM_{2.5}$	PFC	0.800	
	PFN	0.200	
BC	POA	1.000	
OC	PEC	1.000	

a) Molecular weight for gaseous species only

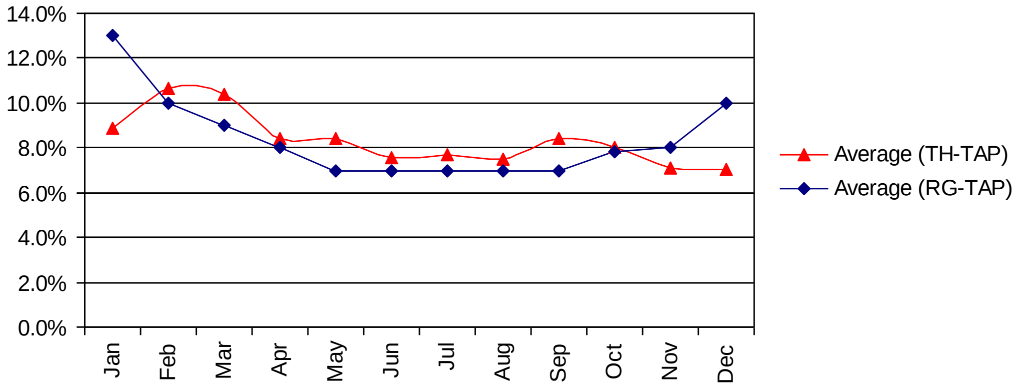
b) NMVOC speciated species follows CB5 mechanism

Temporal Allocation of Emissions

Comparison between temporal profiles developed for Thailand (TH-TAP) (Vongmahadlek *et al.*, 2009) and that suggested by regional emission inventory (RG-TAP)

(Streets *et al.*, 2003) work was made. Similar trends that were found that were high fractions of emissions during November to March, peaking in January to February in RG-TAP and Feb to Mar in TH-TAP. It can be explained that TH-TAP profiles also include the biomass burning. In this work, monthly TAP profiles of TRACE-P were used for coarser domain while that of Vongmahalek were used for fine domain. Daily trends of emissions are assumed as constant and hourly trends follow the hourly profiles suggested in TH-TAP. Figure below show TAP trends used in this work which is presented below

a) Monthly TAP Applied for this Study



b) Hourly TAP Applied for this Study

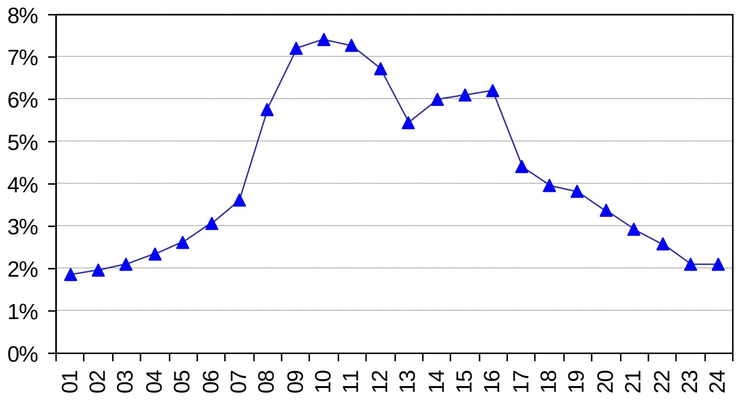


Figure 5.2: Temporal Allocation for Non-Specific Atmospheric Emissions Species Used in this Work

Emission Processing

Emissions processing is used to extract/merge/convert emissions information such as magnitude, spatial, temporal and speciated information that is ready (i.e., right episode as well as specific format required by each model) for input to the model. There is a tool which develop for investigate air quality in Thailand; a so-called THailand Emission Modeling System (THEM) (Vongmahadlek *et al.*, 2012) has been used in this study. Details of input/output to THEM for CAMX application are briefly described in the following

THEM's input:

- Spatial distribution of emissions: Gridded (here, 36 km and 12 km) files of emissions of all interested species (in this case (NOX, CO, NMVOC, SO_2, NH_3, PM_{10}, $PM_{2.5}$, OC, BC, Hg_T, Hg^0, Hg^{2+} and Hg^P)
- Units of input emissions: annual emissions with units of mol/grid (for gaseous) and µg/grid (for particulate)
- Temporal profiles of emissions: Monthly, daily, and hourly
- Chemical speciation: CB05

THEM's output:

- Hourly gridded emissions for each species in binary format, which is readable by CAMx
- Units of output emissions: mol/hour/grid (for gaseous), µg/hour/grid (for particulate)

5.2.2.2. Preparation of Meteorological Input for CAMx

Meteorological parameters are required as key inputs for the air quality model. In this work, MM5 is used to generate meteorological information for CAMx. To convert MM5 output to the format used in CAMx, MM52CAMx tool, which is downloaded from *www.**camx**.com/download/**support**-software.aspx*, was used. Details of input/output of MM52CAMx Tool are presented as follows:

MM52CAMx's input:

- MM5 Output (e.g., MMOUT_DOMAINx)
- Deposition scheme
- CAMx vertical layer

MM52CAMx's output:

- Files of Wind, Temperature, Land use, etc in binary format, which is readable by CAMx

5.2.2.3. Preparation of Initial/Boundary Condition for CAMx

The ICs/BCs of Hg^0 largely affected Hg concentration and deposition, while ICs/BCs of Hg2 and HgP had less impact on Hg concentration and deposition after few modeling time steps (Pongprueksa, 2006). ICs/BCs can be assigned from observation of background situation. In Thailand, the only total Hg atmospheric concentration measured in year 2010 in the northern of Thailand shows daily average values of 2.03 ± 0.15 ng/m3 during 24th – 31st March, 2010 and 2.34 ± 0.44 ng/m^3 during 10th – 18th April, 2010 (Sheu et al., 2013) during intense biomass burning season, which cannot be used as ICs/BCs. It is also favorable to retrieve ICs/BCs from larger domains (i.e. for example, output of global model is often used to be IC and BC). Due to the lack of information for both mentioned case, this study adopted the lower range of IC/BC used for modeling in the case of US for the coarser domain and use output of coarse domain as IC/BC of smaller domain. In Table 5.9, gives the IC and BC adopted for coarse domains used in this work.

Table 5.9: Initial Condition and Boundary Condition Used for Coarse Domain in This Work (Yarwood *et al.*, 2003)

Species (Unit)		**Initial Conditions (IC)**	**Boundary Conditions (BC)**
Hg species	Hg^0 (ppmV)	1.4×10^{-7}	2.5×10^{-7}
	Hg^2 (ppmV)	2.4×10^{-9}	2.5×10^{-8}
	Hg_P (µg/m^3)	3.7×10^{-6}	5.0×10^{-6}
Non-Hg gaseous species	NO (ppmV)	0.00005	
	NO_2 (ppmV)	0.00015	
	O_3 (ppmV)	0.04	
	CO (ppmV)	0.08	
	NH_3 (ppmV)	0.0001	
	SO_2 (ppmV)	0.0002	
	PAR (ppmV)	0.008	
	TOL (ppmV)	0.000001	
	XYL (ppmV)	0.000001	
	HCHO (ppmV)	0.00025	
	ALD2 (ppmV)	0.0001	
	ETH (ppmV)	0.0001	
	PAN (ppmV)	0.00002	
	H_2O_2 (ppmV)	0.001	
	HNO_3 (ppmV)	0.00005	

To prepare ICBC for CAMx, the ICBCPREP Tool, which can be downloaded from www.camx.com/download/support-software.aspx. Details of input/output of ICBCPREP Tool are presented in the following:

ICBCPREP's input:

- ICs/BCs value for all interested species. In this work, ICs/BCs of O_3 precursors, Hg^0, Hg^{2+}, Hg^P were provided (detailed values are in Table 5.9). For other species, CAMx's default, a so-called low-bound value" was automatic assigned (Environ International Corporation, 2011)

ICBCPREP's output:

- ICs/BCs of species by temporal (hourly) and spatial (gridded) dimension in binary format which are readable by CAMx

5.2.2.4. Preparation Photolysis Rate Input for CAMx

To prepare albedo/haze/ozone input files for CAMx, the AHOMAP Tool was used. The details of input/output of AHOMAP Tool are given as follows:

AHOMAP's input:

- A CAMx-ready landuse file (*.lu), which is output from MM52CAMX
- The ozone column was downloaded from ftp://toms.gsfc.nasa.gov/pub/omi/data/monthly_averages/ozone/

AHOMAP's output:

- Albedo, haze, and column ozone intervals. The program assumes a constant haze opacity value for the entire grid

To develop photolysis rate inputs for all CAMx CB05, the TUV Tool was used. The details of input/output of AHOMAP Tool are presented as follows:

TUV's input:

- Albedo, column ozone, and haze opacity intervals defined in AHOMAP

TUV's output:

- Photolysis rate used in CB05 mechanism

5.2.2.5. CAMx Setting

In Table 5.10, the key options used in the CAMx setting are presented. Different options of CAMx simulation setting are provided in the CAMx User Guide (Environ International Corporation, 2011).

Table 5.10: Key Options Used in CAMx Setting

Model Option	Chosen Options (Available Options)
Advection_Solver	PPM (PPM,BOTT)
Chemistry_Solver	EBI (EBI,IEH,LSODE)
PiG_Submodel	None (None,GREASD,IRON)
Probing_Tool	None (None,OSAT,GOAT,APCA,DDM,PA,RTRAC)
Chemistry	True (False, True)
Drydep_Model	ZHANG03 (NONE,WESELY89,ZHANG03)
Wet_Deposition	True (False, True)
ACM2_Diffusion	False (False, True)
TUV_Cloud_Adjust	False (False, True)
Aero_Adjust	False (False, True)
Staggered_Winds	True (False, True)
Super_Stepping	False (False, True)
Gridded_Emissions	True (False, True)
Point_Emissions	False (False, True)

5.2.3. Experiment Conducted in this Study

5.2.3.1. Purpose of the Experiment

The simulation was conducted for this study to obtain objectives 2 and 3, which are “to characterize Hg deposition in Thailand, and to investigate Hg emissions inflow and outflow to and from Thailand, respectively”. To do so, a set of experiments was designed to answer the following questions:

- Assess seasonal variation of Hg deposition,
- Hg deposition sensitivity to emissions,

- Annual inflow/outflow of Thailand emissions to global pool.

Description of Assumptions:

- Seasonal variation: To assess seasonal variation, 4 full months (March, May, August, and November), which are representative of each season, was chosen for simulation
- The inflow of air mass to Thailand was assumed to be equal to the inflow of the mother domain (DM1) to the child domain (DM2). Since there were 4 of one full month of simulation, each of them is representative for 3 months; annual inflow of air mass to Thailand is equaled to 3 times of summation of 4 monthly inflows.
- The outflow of air mass to Thailand was assumed to be equal to the outflow of the child domain (DM2) to the mother domain (DM1). Since there were 4 of one full month of simulation, each of them is representative for 3 months; and annual outflow of air mass to Thailand is equaled to 3 times of summation of 4 monthly outflows.

5.2.3.2. Description of Experiment

The simulation was performed for March, 2010 so that the emissions could be compared to the sampling recorded in Chiangmai province in the northern region of Thailand. Information of this observation is described in Section **5.2.3.3.a.** To assess seasonal variation, episodes were chosen to reflect the seasonal variation of weather change. According to TMD climatologically diagram in year 2010, 4 months have been chosen for investigation seasonal variation, which are March, May, August and November in year 2010. For this experiment, there are 4 simulations were run following 4 chosen episodes, each last one full month with 10 day spinning up. Emissions sources included anthropogenic, biomass open burning and natural sources.

The simulation results of the 4 months for different meteorological parameters but also emissions sources contribution. March is the month that biomass emissions were dominant in the country while May were customarily the month that anthropogenic (i.e., power generation and industrial facilities) emissions were peak.

5.2.3.3. Validation of the Outputs from Conducted Experiments

In Thailand as well as the studied domains, there is still a lack of sampling data on Hg concentration and deposition. The only work is sampling of Hg concentration in year 2010 in Chiangmai, Thailand during Dongsha campaign (Sheu *et al.*, 2013). Sampling of total atmospheric Hg concentration during March and April, 2010 were conducted in Chiangmai province, Northern region of Thailand and values were 2.03 ± 0.15 ng/m^3 during 24th – 31st March, 2010 and 2.34 ± 0.44 ng/m^3 during 10th – 18th April, 2010. It should be noted for CAMx modeling evaluations, because results of CAMx model are hourly grid-based averages, simulating for every grid cells with 12km × 12km resolution. Information of Hg concentration was available just at a specific point in Chiangmai, Thailand, at ground level (less than 10 meter). Thus, a discrepancy of air quality simulation and observation might occur. However, modeling evaluation is important to show how relevant is the trend and magnitude of air concentrations. In addition, air observations can only be detected at the ground level (~10 meters), which is within first level of air quality models. This level is the most concern, in terms of human health and total exposure, because people live here. As O_3 and PM_{10} is an important reactant of Hg, evaluation of O_3 and PM_{10} concentration was also investigated by comparison of simulated results with observation obtained from the PCD.

5.3. Results and Discussions

5.3.1. Concentration/Deposition of Hg Reactants Species

5.3.1.1. O_3 Concentration

The spatial distribution of O_3 concentration shows seasonal variations. In general, monthly O_3 concentration is in range of 10-35 ppb which was agreement with other works of O_3 concentration in Thailand. In March, O_3 concentration was high in the northern of Thailand due both to high emission intensity of this season and inflow originated from Northeastern brings pollutants from southern China to the northern of Thailand. Among 4 seasons of March, May, August and November, O_3 concentration is high during dry season (March and November) and low during wet season (May and August). It is due to warm temperature in dry season yield favor condition for O_3 formation. In additional, low concentration of O_3 in wet season could be result of wet deposition.

A time series analysis of O_3 concentration for 5 O_3 station for each of the 4 months (shown in Appendix C) showed underestimation and less variation as compared to observation. Possible reasons are that crude resolution of emissions grid as well as modeling grid that makes emissions of point sources was diluted. It can be solved by effort of point-source identifying and its characteristic such as stack height, stack parameters are very important and should be obtained and include in future work. Observation site available in Thailand was mostly urban and closed to emissions sources.

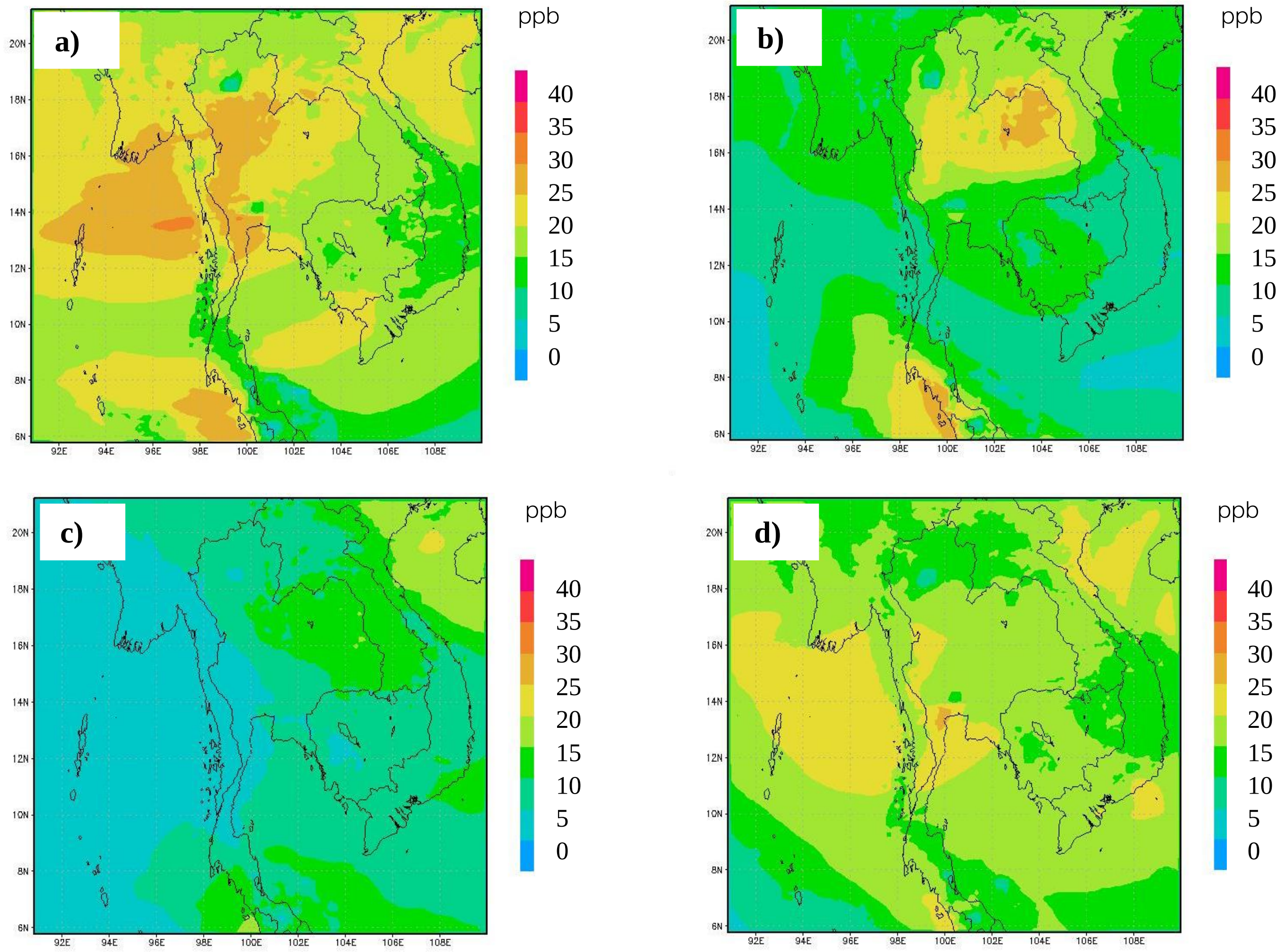


Figure 5.3: Monthly Average of O_3 Concentration in a) March b) May, c) August, and d) November

5.3.1.2. PM Concentration

The spatial distribution of PM_{10} concentration shows strong seasonal variations (Figure 5.5). In general, monthly PM_{10} concentration is in range of 20 to above 40 $\mu g/m^3$. For all seasons, PM_{10} is tended to high in the greater Bangkok metropolitan as well as northern and northeastern regions of Thailand. PM_{10} concentration during dry seasons of March and November was significant higher compared to that during May and August.

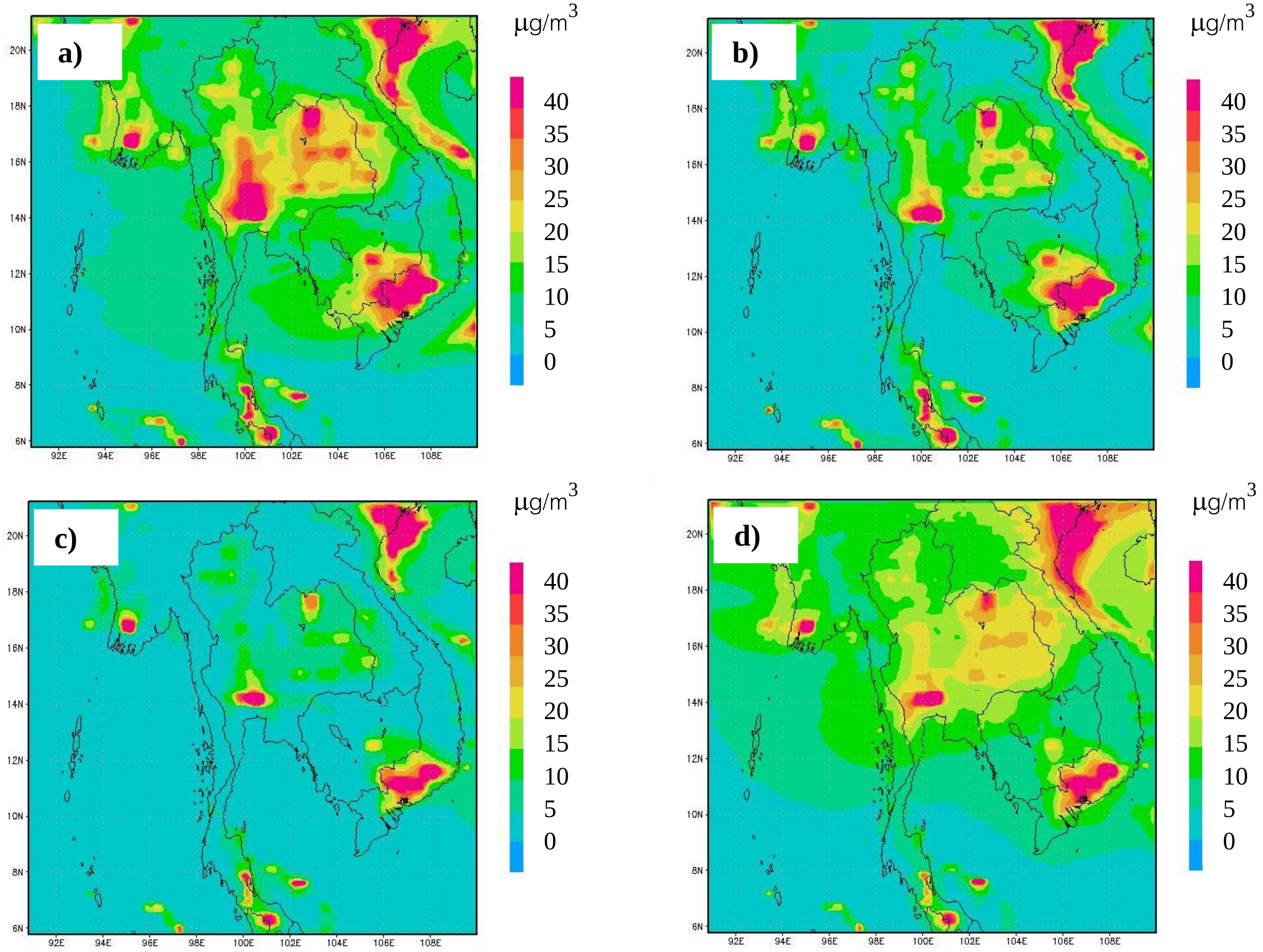


Figure 5.4: Monthly Average of PM10 Concentration in a) March, b) May, c) August, and d) November

5.3.2. Concentration/Deposition of Hg Species

5.3.2.1. Hg Concentration

The average monthly Hg concentrations ranged from 1.7 ng/m^3 to 2.6 ng/m^3. During the dry season, March and November had a higher Hg concentration, while the wet months of May and August have a lower concentration. Among the 3 species, Hg^0 has high concentration (up to 2.3 ng/m^3), accounted for up to 80% - 90% of total Hg atmospheric concentration, following by Hg^{2+} which concentration is up to 0.3 ng/m^3 account for 8% - 15%. Atmospheric concentration of Hg^P is very less (approximately 10^{-3} ng/m^3) of total Hg atmospheric concentration. This is consistent with the finding’s output from the global model.

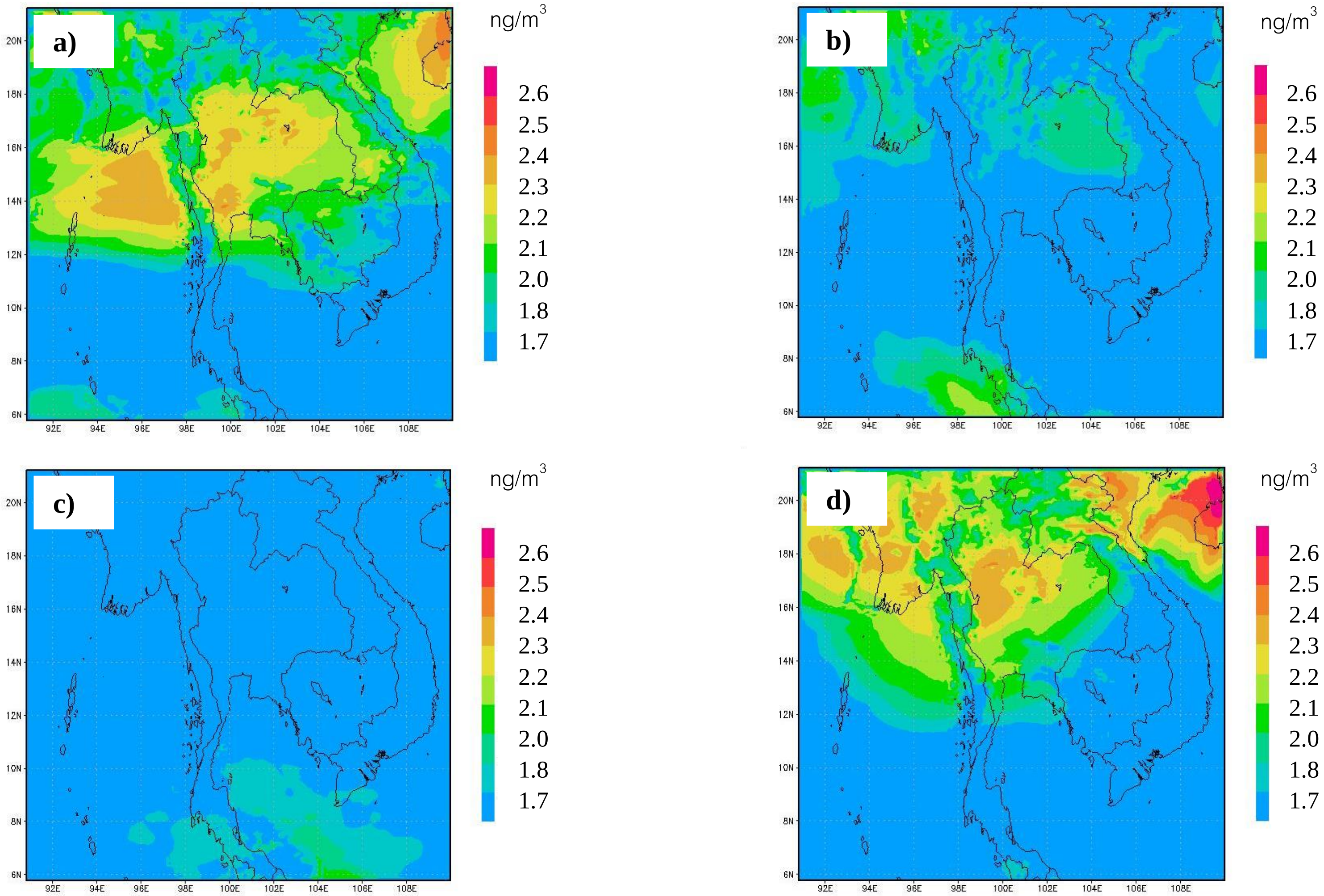


Figure 5.5: Monthly Average of Total Hg Concentration in a) March, b) May, c) August, and d) November

5.3.2.2. Hg Deposition

Dry Deposition

The monthly accumulated dry deposition ranged from 0.4 – 2 g/km^2/month, mostly located near the coastal of Thailand. Among 3 species, dry deposition of Hg^0 is dominant due to high Hg^0 concentration in the atmosphere while dry deposition of Hg^{2+} and Hg^P. In terms of seasonal variation, dry deposition of Hg^0 is relatively high in March and May, which is reasonable by the high Hg^0 concentration during those months. During wet season, dry deposition is low during May and almost none in August. Dry deposition of Hg^{2+} is highest in August and low in other months. Dry deposition of Hg_P is also insignificant during all the months, mostly caused by dry deposition velocity of $Hg_{P.}$

Wet Deposition

The monthly accumulated wet deposition is high in the rainy season (i.e. May and August) and wet deposition map has same pattern of monthly accumulated precipitation map confirm scientific literature about the influence of precipitation to wet deposition both magnitude and spatial pattern. Among species, Hg^{2+} wet deposition is significant, especially during rainy season (i.e., May and August). Hg^0 wet deposition is significant less for all seasons, mostly due to the less water absorption ability.

Total Deposition

The monthly accumulated Hg deposition was within 0.4-2.4 g/km^2, which are the annual accumulated results from 4.8 - 28.8 g/km^2/year. It is not far from 20-50 g/km^2/year from literature review, though slightly lower. Hg deposition has less seasonal variation. Dry deposition play an important role for Hg deposition in Thailand. Dry Hg deposition is occurred in the upper part and central regions of Thailand while wet deposition is occurred in location of high precipitation and along the coastal of Thailand. According to mass analysis, total Hg deposition of domain 2 during simulation months was 15.39 Mg, 13.94 Mg, 17.14 Mg, and 15.33 Mg for March, May, August, and November 2014. The annual total Hg deposition of domain 2, defined as 3 times of total 4 month deposition, equaled 185.4 Mg.

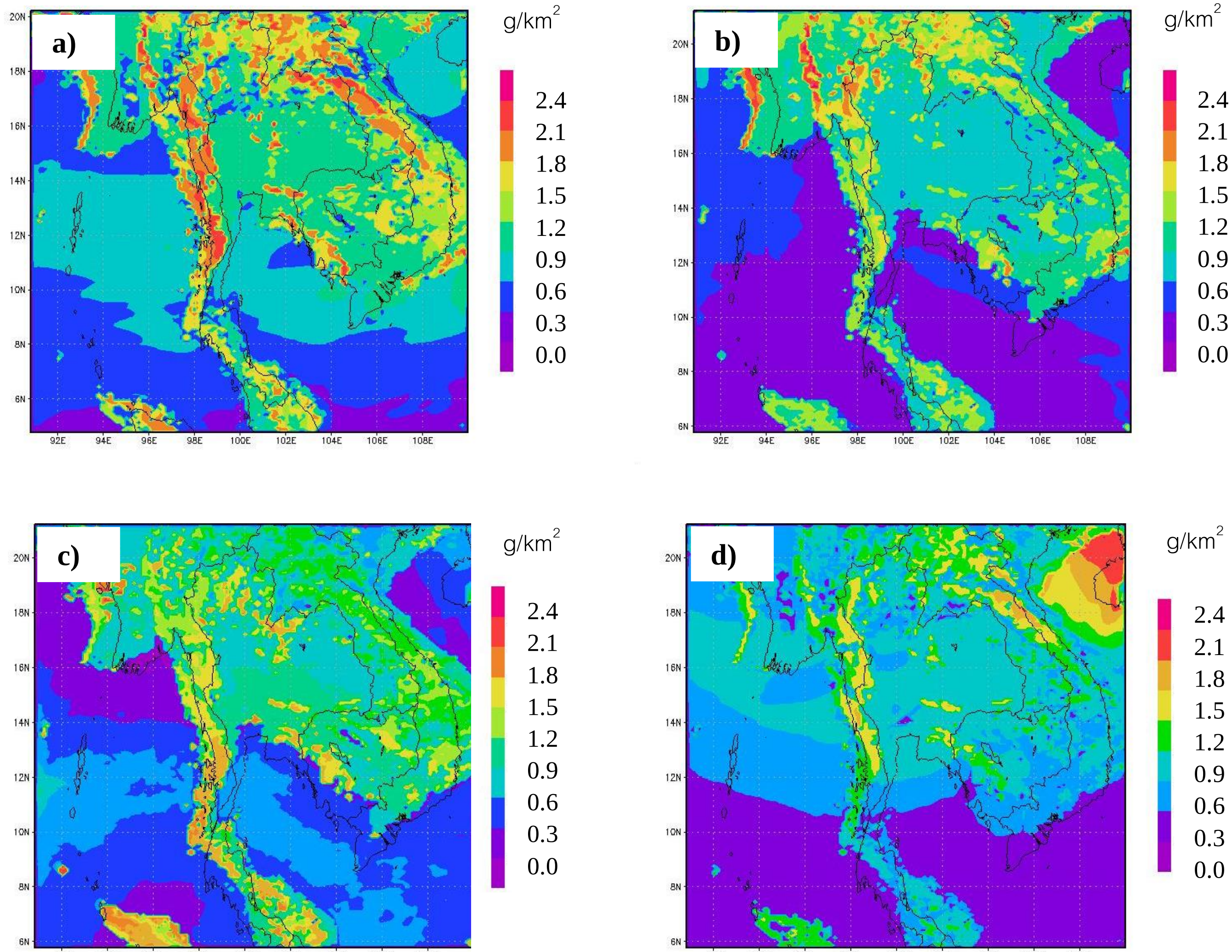


Figure 5.6: Monthly Average of Total Hg Dry Deposition in a) March, b) May, c) August, and d) November

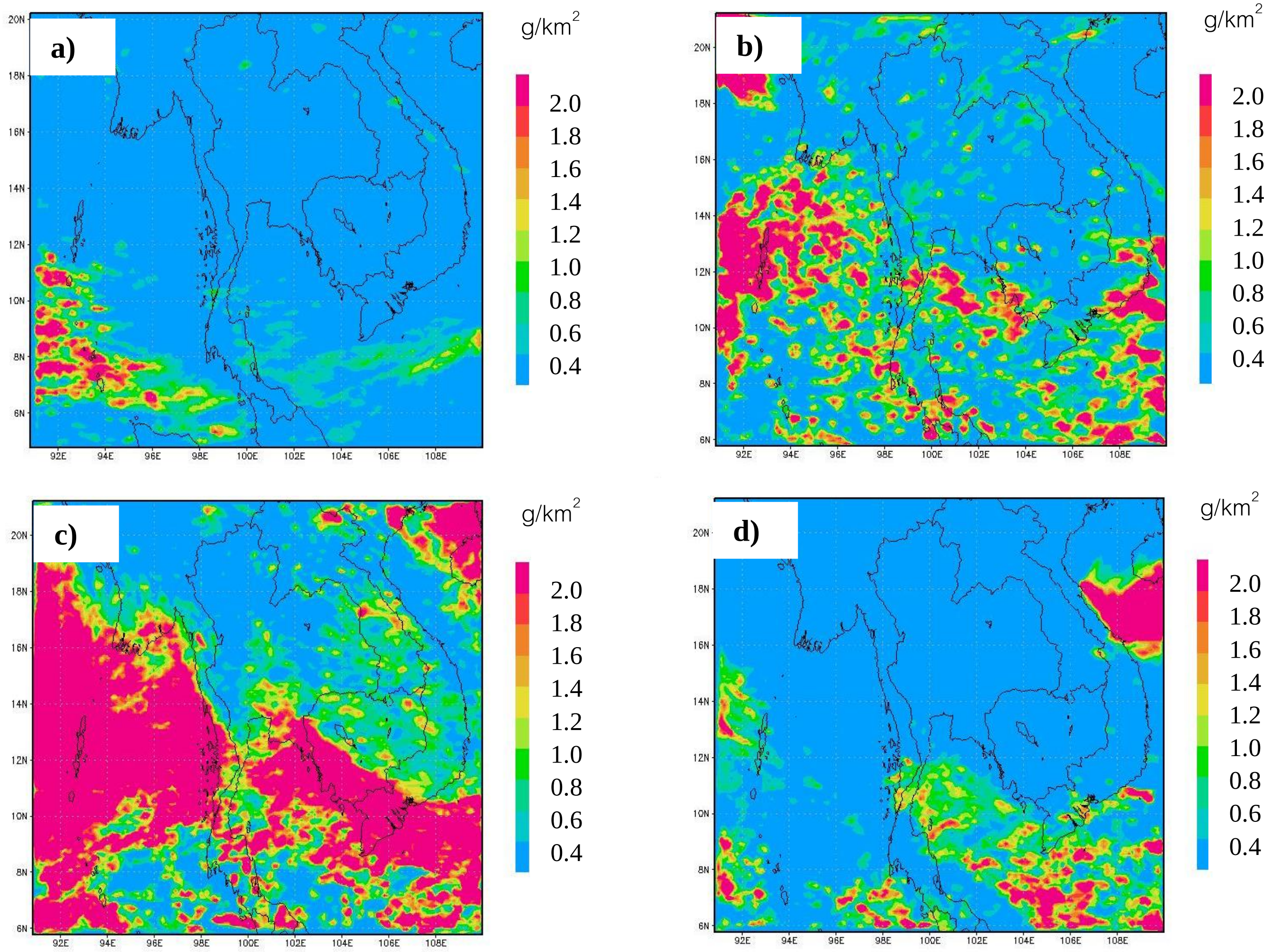


Figure 5.7: Monthly Average of Total Hg Wet Deposition in a) March, b) May, c) August, and d) November

5.3.3. Summary of Simulation Experiment-Based Case

In this experiment, rough comparisons as well as seasonable variations of atmospheric concentration and deposition of Hg species in relation to its reactants are presented. Monthly O3 concentration is ranging from 18-30 ppb, respectively. Hourly time series comparison with observation indicated that O3 concentration from simulation is underestimated, mostly in the Northern. It was due mainly to concentration of O3 precursors were underestimated, possibly during biomass intensive period.

Monthly Hg concentrations are up to 1.8 ng/m3 and seasonal variations of Hg concentration follows the pattern of O3 concentration. Hg deposition is up to 2.4 g/km2/month which approximately up to 30 g/km2/year. Due to lack of observation of ambient data, modeling output was roughly compared with other modeling work and it was in the same order of magnitude.

Possible reasons for the uncertainty of the concentrations of atmospheric species may be:

- Under-estimation of emissions of both criteria emissions and Hg emissions which cause underestimation of Hg reactant such as O3 and PM. Similar conclusion had been found for some other modeling work used similar database (work on INTEX-B and Hg emissions)
- Crude resolution of the emissions grid as well as the modeling grid that dilutes emissions of the point sources. It can be possibly solved by effort of point-source identifying and its characteristic such as stack height, stack parameters are very important and should be obtained and include in future work.
- Observation sites are mostly urban and close to emission sources.

5.3.4. Sensitivity of Hg Deposition to Hg Emissions

To assess Hg deposition to Hg emissions, another set of simulations which were run disabled Hg emissions inside domain 2 and enabled just emissions only in domain 1. Average monthly Hg concentrations are ranging from 1.5 ng/m^3 to 2.3 ng/m^3, which is not significant less than 1.8 ng/m^3 to 2.6 ng/m^3. Seasonal variation indicated that during dry season, March and November had a higher Hg concentration, while the wet months of May and August have a lower concentration. In addition, seasonal variation of deposition indicated that deposition density was quite similar to the base case. However, mass balance analysis showed that total

Hg deposition in domain 2 was 157.9 Mg, 14.8% less than 185.4 Mg which as total Hg deposition in domain 2 in base case. The finding confirms that most of atmospheric Hg concentration and deposition in Thailand (i.e. domain 2) was from mass inflow.

5.3.5. Annual Inflow/Outflow of Thailand Emissions to Global Pool

The inflow and the outflow of Hg species were analyzed. The transport budget of Hg^0 is relatively small and positive for all simulation months, indicating net transport of Hg speciated emissions out of the domain, while that of Hg^{2+} and Hg^P is relatively high and negative, indicating net removal within the domain. High deposition of both Hg^{2+} and Hg^P indicated that the possible risk of Hg accumulated in ecosystems which cause adverse effects to human health and ecosystems.

Table 5.11: Seasonal Variations of Hg Mass Budget in Thailand Domain in Year 2010

	March			**May**			**August**			**November**		
	Hg^0	**Hg^{2+}**	**Hg^P**	**Hg^0**	**Hg^{2+}**	**Hg^P**	**Hg^0**	**Hg^{2+}**	**Hg^P**	**Hg^0**	**Hg^{2+}**	**Hg^P**
Initial Hg Mass (Mg)	14.9	1.6	1.2	14.7	1.7	1.1	14.9	1.4	0.2	15.1	1.4	0.2
Final Hg Mass (Mg)	15.2	1.4	1.1	15.4	1.3	0.9	15.1	1.3	0.1	15.4	1.1	0.1
Emissions (Mg)	1.94	0.8	0.4	1.48	1.1	0.5	1.34	1.1	0.5	1.34	1.1	0.5
Deposition (Mg)	0.19	14.5	0.7	0.34	12.8	0.8	0.14	16.2	0.8	0.13	14.3	0.9
Transport Budget (Mg)	2.05	-13.90	-0.40	1.84	-12.10	-0.50	1.40	-15.20	-0.40	1.51	-13.50	-0.50
Net Transport Budget (Mg)	-12.25			-10.76			-14.2			-12.49		

5.4. Chapter Summary

This chapter describes the investigation of Hg concentrations and deposition in Thailand using air quality model CAMx. Emissions and meteorological inputs have been prepared to CAMx using several supported tools developed by CAMx communities. Simulations of different months showed that relatively high Hg concentration, mostly located in the northern of Thailand, is found in March and November, 2010. It is partly due to the high Hg emissions resulting from biomass burning activity in the regions during these periods. Of note that output of this work was not directly performed by in pair comparing with observations because firstly, there were no long term records of Hg concentration or deposition in study domain. Monthly mean total Hg concentrations ranged between 1.7-2.6 ng/m^3 which is not far from 1.7-2.0 ng/m^3 for mean yearly total Hg concentration from GEOS_Chem output (Holmes et al., 2010) and 2.04 – 2.43 ng/m^3 from samplings in the northern of Thailand during March and April, 2010 (Sheu et al., 2012). Monthly accumulated Hg deposition was up to 2.4 g/km^2/month, which is approximately 30 g/km^2/year in range with 20-50g/km^2/year found in HTAP (2010). Sensitivity test of Hg deposition on emissions by disable Hg emissions inside domain 2 indicated that most of Hg concentration and deposition inside Thailand domain caused in mass inflow. The inflows and outflows of Hg species were analyzed. Transport budget of Hg^0 is relatively small and positive for all simulation months, indicating net transport of Hg speciated emissions out of the domain while that of Hg^{2+} and Hg^P is relatively high and negative, indicating net removal within the domain.

CHAPTER 6
CONCLUSIONS

6.1. Summary of Findings

This study was conducted to investigate the characteristics of Hg deposition in Thailand using air quality modeling. To do so, 3 key components including emissions inventory and processing, MM5 meteorological model and CAMx air quality modeling were investigated. Hg emissions inventory has been updated for Thailand for natural, anthropogenic sources as well as biomass open burning. Meteorological characteristics as output of MM5 was chosen from sensitivity test. Hg concentration and deposition characteristic was investigated for seasonal variation and sensitivity of deposition to emissions as well as inflow and outflow of emissions using air quality model of CAMx. Following conclusions can be draw for each chapter

Chapter 3 described how objective 1 of this study was met by characterizing atmospheric Hg emissions in Thailand. In this chapter, atmospheric Hg emissions were estimated for Thailand in year 2010 using bottom up approach for natural source, anthropogenic sources as well as biomass open burning. Source specific activity data were collected locally and emissions factors were either from local sources or adapted from literature review with proper adjustments to well reflect emitting behaviors of various sources in Thailand. It was found that in year 2010, total atmospheric Hg emissions in year 2010 were 20,495.2 kg, which 79.0% from natural sources, 19.7% from anthropogenic sources, and 1.2% from biomass open burning. Within Hg speciation, Hg^0, Hg^{2+} and Hg^P accounted for 91.7 %, 6.5%, and 7.8 % respectively. Key sources of emissions were coal combustion in industrial facilities, followed by zinc production and lignite combustion in thermal power plants. GIS maps of spatially distributed emissions presented relatively high dense anthropogenic emissions in the central and eastern regions, where most of industrial activities happen while biomass open burning emissions were from northern and northeastern regions due to biomass burning activities.

Chapter 4 described the air meteorological modeling. As one of the key inputs for air quality modeling, robustness of meteorological outputs is crucial in assessing emissions' fate.

Meteorological parameters, such as wind speed, wind direction, temperature, and radiation, contribute highly to uncertainties of the air quality model. These uncertainties can be much reduced if the applications choose appropriate physical options. This chapter has analyzed meteorological condition in Thailand to choose episode that representative for investigate seasonal variation of Hg deposition. It is 3 physical combined options were chosen for sensitivity test. In general, all options capture the temporal variation of meteorological parameters in Thailand which influence by monsoon. The comparison with 3 hourly data with Thai Meteorological Department, temperature at 2m is underestimated up to 2^0C and wind speed is overestimated and wind direction is high uncertainties. It is found that there is no combined options are best throughout Thailand for all year long. Among 3 investigated physical options, the combination of Grell, MRF, Simple ice, Cloud radiation scheme, and Five layer soil model have better agreement with observation compared to other options.

Chapter 5 discussed the investigation of concentrations and deposition in Thailand using air quality model CAMx. To do so, emissions inventory used to be input for model was chosen from different sources of literature. Emissions and meteorological inputs have been processed to CAMx using several supported tools developed by CAMx or local review. Simulations of different months showed that relatively high Hg concentration, mostly located in the northern of Thailand, is found in March and November, 2010. It is partly due to the high Hg emissions resulting from biomass burning activity in the regions during these periods. Hg deposition has less seasonal variation. Dry deposition play an important role for Hg deposition in Thailand. Dry Hg deposition is occurred in the upper part and central regions of Thailand while wet deposition is occurred in location of high precipitation and along the coastal of Thailand. Annual total Hg deposition of domain 2, defined as 3 times of total 4 month deposition, equaled 185.4 Mg. Indirect comparisons between the simulation in this study and the global simulation, and with limited observations show reasonable agreement. Sensitivity test of Hg deposition on emissions by disable Hg emissions inside domain 2 indicated that most of Hg concentration and deposition inside Thailand domain caused in mass inflow. Inflow and out flow of Hg species were analyzed. Transport budget of Hg^0 is relatively small and positive for all simulation months, indicating net transport of Hg speciated emissions out of the domain while that of Hg^{2+} and Hg^P is relatively high and negative, indicating net removal within the domain.

6.2. Uncertainties of the Findings

Uncertainties of the models, especially air quality models, always exist. They are resulted from emissions inventory, meteorological and air quality model itself. They can be listed as following

- Emission inventory development: Lack of sampling data to develop locally based emission factors, and uncounted emissions sources.
- Emission model: Inappropriate assumptions of horizontal and vertical spatial, temporal and speciated emissions distributions. It is possible for computational errors to occur in this stage
- Meteorological model: Sources of huge uncertainties due to data input (large scale to small scale), physical options chosen are the best feasible options, but do not totally fit the large studied domain for all parameters and time periods
- Air quality model: uncertainties from choosing chemical schemes. In fact Hg chemical reactions and their rates have not yet been fully understand and, still controversial.

6.3. Recommendation for Future Studies

To reduce the uncertainties listed above, the following future studies are suggested

Emission Inventory:

- Surveys are needed to examine Hg contents in different fuels and materials.
- Stack sampling or mass balance studies should be conducted to determine mercury emission factors, especially for large point sources.
- Speciation of Hg emissions need to be investigated by measurements because it influence Hg’s fate in the atmosphere

Meteorological Model:

- Further evaluations of all available stations in Thailand should be included. Other sensitivity runs are also suggested to seek for better representative meteorological profiles in the studied domains.
- Other meteorological models, such as RAMS or WRF, can be investigated

Air Quality Model:

- Efforts on emission processing should include the treatment of point sources and other elevated sources. In addition, local data on temporal variation of each sources type as well as emissions speciation will help to increase models' reliability.
- Updated datasets of primary pollutants (i.e., gaseous and particulate matter) should be used.
- Further sensitivity tests on different input of emissions should be conducted to investigate the contribution of each type of sources or the influence of initial and boundary conditions to atmospheric Hg concentration and deposition in Thailand.
- Efforts to seek for monitoring data on atmospheric Hg concentrations and deposition should be included for better model evaluation.

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APPENDIX A

INFORMATION RELATED TO THE DEVELOPMENT OF ATMOSPHERIC HG EMISSIONS IN THAILAND

A.1) Classification of Industrial Facilities in Thailand

A.2) Combustion Technology of Industrial Facilities in Thailand

A.1) Classification of Industrial Facilities in Thailand

DIW-107 Types	Description	TSIC_9 Types
1	Factories engaged in tea or tobacco preservation	3141
2	Factories engaged in other agricultural production	3909
3	Factories related to rock, gravel, sand, or soil for construction	2901
4	Factories related to animals other than aquatic animals	3111
5	Factories related to milk and dairy products	3112
6	Factories related to aquatic animals	3114
7	Factories related to oil from plants or animals or animal fats	3115
8	Factories related to vegetables, plant and fruits	3113
9	Factories related to plant seeds or plant bulbs	3116
10	Factories related to food from flour	3117
11	Factories related to sugar made from sugar cane, beech, stevia or other sweetening plants	3118
12	Factories related to tea, coffee, cocoa, chocolate or sweets	3119
13	Factories related to food seasoning or food ingredients	3121
14	Factory engaged in ice making, ice cutting, ice sawing, ice crushing or ice grinding	3121
15	Factories engaged in animal feeds	3122
16	Distilleries or liquor blending houses	3131
17	Factories producing ethyl alcohol (excluded production from extracted sulfide for pulp mill)	3131
18	Factories making liquor from fruits or other types of wine (excluded those related to malt and beer as per Factiry Type 19)	3132
19	Factories engaged in production of malts or beers	3133
20	Factories making non-alcoholic drinks or soft drinks	3134
21	Factories related to tobacco, compressed tobacco, pipe tobacco, chewing tobacco or snuff	3142

DIW-107 Types	Description	TSIC_9 Types
22	Factories related to textiles, yarn, or fiber (excluded asbestos)	3211
23	Factories related to textile products (excluded apparel)	3212
24	Factories weaving fabric, lace or apparel with yarn or fiber, or bleaching and dyeing or finishing of fabric, lace or apparel woven with yarn or fiber	3213
25	Factories making garments or carpets by means of weaving, intertwining, embroidering, or interlacing (excluded those made of rubber or plastic which are not linoleums)	3214
26	Factories related to ropes, meshes, fishnets, seines	3215
27	Factories related to non-woven or non-knitted products	3219
28	Factories related to apparel (excluded shoes)	3220
29	Factories fermenting, eviscerating, roasting, pulverizing or grinding, tanning, polishing and finishing, embossing or paint-coating of animal hides	3231
30	Factories combing, cleaning, bleaching, dyeing, polishing or dressing of fur	3231
31	Factories making carpets or utensils from leather or fur	3233
32	Factories manufacturing products or parts of products (excluded apparel or shoes)	3233
33	Factories producing shoes or parts of shoes (whicg are not made of wood, skimmed block rubber, extruded rubber or extruded plastic)	3240
34	Factories related to wood	3311
35	Factories producing containers or utensils from bamboos, rattans, straws, reeds, or water hyacinths	3312
36	Factories related to wood or cork products	3319

DIW-107 Types	Description	TSIC_9 Types
37	Factories producing household furnishings or furniture for buildings from wood, glass, rubber, or metals (which are not extruded plastic), including their parts	3320
38	Factories producing pulps or paper	3411
39	Factories producing packages from all kinds of paper or from fiberboard	3412
40	Factories related to pulps or cardboards	3419
41	Factories engaged in printing, document file making, binding, making a cover or decorating printed matters ,making metal mold	3420
42	Factories related to chemical products, chemical substances, or chemical materials (which are not fertilizers)	3511
43	Factories related to fertilizers or pesticides	3512
44	Factories producing synthetic resin, elastomer, plastic, or synthetic fiber (which are not fiber glass)	3513
45	Factories related to paints, varnishes, shellacs, lacquers, or patching or caulking products	3521
46	Factories related to medicines	3522
47	Factories related to soap, cosmetics, or body beautifications	3523
48	Factories related to specified chemical products	3529
49	Petroleum refinery	3530
50	Factories related to petroleum, coal, or lignite products	3540
51	Factories producing, repairing, retreading, or remolding inner or outer tyres for vehicles driven by machines, manpower, or animals	3551
52	Factories related to rubber	3559
53	Factories related to plastic products	3560
54	Factories producing glass, fiberglass, or glassware	3620

DIW-107 Types	**Description**	**TSIC_9 Types**
67	Factories related to machineries, machinery components or accessories for woodwork or metalwork	3823
68	Factories manufacturing, assembling, modifying, or repairing machineries for paper industry, chemical industry, food industry, pipe production, printing, cement or clay productions, construction, mining, petroleum drilling or oil refinement, including their components or accessories	3824
69	Factories producing, assembling, modifying, or repairing calculators, accounting machines, punching machines, digital or analog computers or associated electronic data processing equipment or accessories, typewriters, weighing machines (that are not used in the scientific laboratory), copiers (which are not the photocopiers), including their components or accessories	3825
70	conditioners or air ventilators, sprinklers, refrigerators or their components, vending machines, cleaning machines, washing machines, dry cleaning machines, ironing machines, sewers, mechanical transmitters, elevators, cranes, lifts, escalators, trucks, tractors, industrial trailers, stackers, furnaces, kilns, oven or stove that are not electrical-activated, including their components and equipment	3829
71	Factories manufacturing, assembling, modifying, or repairing electric machineries or products listed in Factory Type 70, electric motors, electrical generators, transformers, electric switches or controls, electric panel instruments, electric diverters, electric transmitters, electric control machines, or electric welders	3831

DIW-107 Types	Description	TSIC_9 Types
81	Factories related to scientific or physical equipment or instruments	3850
82	Factories manufacturing tools or instruments for eyes or visual acuity test, lenses, light-activated tools or instruments, or photocopiers	3850
83	Factories producing or assembling timepieces or parts of watches or timepieces	3850
84	Factories related to diamonds, precious stones, gold, silver, alloy of gold, silver, and copper, or gems	3901
85	Factories producing or assembling musical instruments including their parts or components	3902
86	Factories producing or assembling equipment or apparatus for sports, body exercise, billiard, bowling, fishing, as well as their parts or components	3903
87	Factories related to playthings, tools or devices that are not listed in other Factory Types	3909
88	Factories producing, transmitting, or distributing electrical power	4101
89	Factories producing gas (which is not natural gas), transmitting, or distributing gas.	4102
90	Factories supplying water, purifying water or distributing water to buildings or industrial facilities	4200
91	Factories related to a packaging process (which does not involve any production process)	3909
92	Cold or refrigerated storage	3909
93	Shoes or leather repairing factory	3240
94	Electrical appliances, domestic or personal appliances repairing factory	3909

DIW-107 Types	Description	TSIC_9 Types
72	Factories manufacturing assembling, modifying, or repairing radio receivers, television receivers, transmitters or sound recorders, phonographs, dictation recorders, tape recorders, video players, video recorders, discs, recorded magnetic tapes, cord or cordless telephones and telegraphs, radio transmitters, television transmitters, transceivers or sensory devices, radars, semi-conductor or related sensitive semi-conductor devices, fixed or variable electronic capacitors or condensers, radiographic machines or radiographic tubes, fluoroscopic machines or fluoroscopic tubes, or X-ray machines or X-ray tubes, as well as manufacturing equipment for such electronic devices	3832
73	Factories manufacturing, assembling, or modifying electric tools or utensils not listed in any sequence including their components or equipment	3833
74	Factories related to specified electrical appliance or equipment	3839
75	Factories related to ship or shipwork	3841
76	Factories related to trains, streetcars, or cable cars	3842
77	Factories related to automobiles or trailers	3843
78	Factories related to motorcycles, tricycles or bicycles	3844
79	Factories related to aircrafts or hovercrafts	3845
80	Factories manufacturing, assembling, modifying, or repairing wheeled vehicles propelled by human or animal powers (that are not bicycles), including their components or equipment.	3849
81	Factories related to scientific or physical equipment or instruments	3850
82	Factories manufacturing tools or instruments for eyes or visual acuity test, lenses, light-activated tools or instruments, or photocopiers	3850

DIW-107 Types	**Description**	**TSIC_9 Types**
95	Factories engaged in servicing motor vehicles, trailers, tricycles, bicycles, or their components	3849
96	Factories repairing clocks, timepieces, or accessories made of diamond, precious stone, gold, white gold, silver, alloy of gold, silver, and copper, or gems	3909
97	Repairing factories (which are not mentioned in any Factory Type)	3909
98	Factories for laundering, dry-cleaning, cleaning, ironing, pressing, or dyeing of apparel, carpet, or fur	3909
99	Factories producing, repairing, modifying, or changing the form of firearms, ammunitions, explosives, weapons or other articles capable of killing, destroying or disabling in the same manner as firearms, ammunitions or explosives, including their components	3909
100	Factories engaged in dressing or changing appearance of any product or its components (without any production involved)	3909
101	Central waste treatment plant	3909
102	Factories producing and/or distributing steam	3909
103	Factories related to salt	3909
104	Factories manufacturing, assembling, modifying, or repairing boilers or boiling container using liquid or gas to conduct heat, pressure vessels, including their components or equipment	3909
105	Factories related to sorting or land filling of industrial wastes	3909
106	Factories engaged in recycling of industrial wastes or used industrial products	3909

DIW-107 Types	Description	TSIC_9 Types
107	Factories making CDs, products for electronic data, sound, and image recording readable by a device requiring high-powered light sources such as laser, a disc, a magnetic picture recording tape, a magnetic sound recording tape, and a magnetic picture and sound recording tape, be it in the form of recorded products, re-recordable products, or non-recorded products	3909

A.2) Combustion Technology of Industrial Facilities in Thailand

ISIC Sector	Fuel Type	Equipment
Food and Beverage	Bituminous	Imported Coal Boiler
	Lignite	Lignite Boiler
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Boiler
	Fuel Wood	Fuel Wood Boiler
	Bagasse	Bagasse Boiler
	Paddy Husk	Paddy Husk Boiler
	Natural Gas	Natural Gas Boiler
Textile	Lignite	Lignite Boiler
	Natural Gas	Natural Gas Boiler
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Boiler
Wood	LPG	LPG Dryer
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Dryer
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Dryer
	Fuel Wood	Fuel Wood Dryer

ISIC Sector	Fuel Type	Equipment
Paper	Lignite	Lignite Boiler
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Boiler
	Bituminous	Import Coal Boiler
Chemical	Anthracite	Coal Chemial Process
	Bituminous	Coal Chemial Process
	Coke	Coal Chemial Process
	Other Coal	Coal Chemial Process
	Lignite	Coal Chemial Process
	Natural Gas	Natural Dryer Chemical Process
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Dryer
	Fuel Wood	Fuel Wood Dryer
Non-Metalic	Bituminous	Coal Kiln
	Coke	Coke Oven
	Lignite	Coal Kiln
	Natural Gas	Natural Gas Kiln
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine

ISIC Sector	Fuel Type	Equipment
Non-Metalic	Kerosene	Kerosene Furnace
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Kiln
	Fuel Wood	Fuel Wood Boiler
	Paddy Husk	Paddy Husk Boiler
	Anthracite	Coke Oven
	Other Coal	Coal Kiln
Basic Metal	Anthracite	Coke Oven
	Bituminous	Coke Oven
	Coke	Coke Oven
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Dryer
	Lignite	Lignite Boiler
	Other Coal	Coke Oven
Fabricated Metal	Natural Gas	Natural Dryer
	LPG	LPG Furnace
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Furnace
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Dryer
	Anthracite	Coke Oven

ISIC Sector	Fuel Type	Equipment
Other	Anthracite	Coke Oven
	Lignite	Lignite Boiler
	LPG	LPG Boiler
	Gasoline	Heavy Duty Gasoline Engine
	Kerosene	Kerosene Boiler
	Diesel	Heavy Duty Diesel Engine
	Fuel Oil	Residual Oil Boiler
	Bituminous	Imported Coal Boiler
	Other Coal	Imported Coal Boiler
	Coke	Coke Oven

APPENDIX B

INFORMATION RELATED TO AN APPLICATION OF METEOROLOGICAL MODEL

B.1). Example of Meteorological Data – Ground Station

B.2). Example of Meteorological Data – Rawinsonde Data

B.3). Diurnal Trends of Observation and Simulation Data

B.1). Example of Meteorological Data – Ground Station

CLIMATOLOGICAL DATA FOR THE PERIOD 2010-2010

Station	MAE HONG SON	Elevation of station above MSL	267.74 Meters
Index Station	48300	Height of barometer above MSL	278.48 Meters
Latitude	19.18.0 N	Height of Thermometer above ground	1.20 Meters
Longitude	97.50.0 E	Height of wind vane above ground	19.68 Meters
		Height of rainguage	0.80 Meters

Elements		N-Years	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Annual
Pressure(hPa)	Mean	1	1014.09	1012.53	1009.97	1007.31	1005.10	1005.91	1006.07	1006.22	1007.59	1008.59	1012.06	1010.54	1008.83
	Mean Daily Range	1	7.11	7.95	8.17	7.85	6.52	5.16	4.84	5.02	5.76	5.59	6.76	6.23	6.41
	Ext.Max.	1	1020.94	1018.16	1017.65	1013.64	1011.53	1010.36	1010.85	1011.72	1012.77	1017.69	1018.51	1016.62	1020.94
	Ext.Min.	1	1007.29	1006.26	1001.40	1000.36	997.45	998.94	1000.03	998.08	1000.92	1002.54	1005.04	1001.78	997.45
Temperature(Celcius)	Mean Max.	1	31.2	33.9	37.1	41.3	39.4	35.3	34.0	32.5	33.4	32.6	30.8	29.0	34.2
	Ext.Max.	1	33.5	36.0	39.3	43.4	44.0	39.7	36.8	36.0	35.5	36.6	32.5	30.6	44.0
	Mean Min.	1	16.5	15.1	20.0	25.2	25.6	24.0	23.3	22.7	22.5	21.3	16.9	18.1	20.9
	Ext.Min.	1	11.9	12.4	15.6	21.9	23.0	22.0	21.8	21.3	20.9	15.9	13.5	12.1	11.9
	Mean	1	22.6	23.2	28.1	32.5	31.9	29.2	28.1	27.3	27.5	26.7	23.7	22.3	26.9
Dew Point Temp.(Celcius)	Mean	1	16.5	14.1	16.6	18.9	22.1	24.0	24.2	24.1	24.0	23.2	19.5	18.4	20.5
Relative Humidity(%)	Mean	1	72	61	53	48	60	75	81	84	82	82	79	80	71.4
	Mean Max.	1	93	89	78	70	78	89	93	94	94	94	95	95	88.6
	Mean Min.	1	42	29	30	25	38	55	60	67	63	62	54	55	48.4
	Ext.Min.	1	34	18	19	20	24	36	50	51	52	43	39	40	18.0
Visibility(Km.)	Mean	1	10.0	8.5	3.7	6.1	11.5	11.6	11.0	10.3	10.0	10.1	8.3	8.5	9.1
	07.00LST	1	4.8	5.5	2.3	4.5	10.5	10.0	9.5	8.5	7.2	6.5	2.0	2.2	6.1
Cloud Amount(1-10)	Mean	1	2.0	1.0	0.0	1.0	5.0	8.0	8.0	8.0	8.0	7.0	2.0	3.0	4.4

Elements		N-Years	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Annual
Wind (Knots)	Prev.Wind	1	SE	SE	S	S	S,S	S	S,SW	S	SE	N,SE	E,SE	SE	-
	Mean	1	0.6	0.9	0.7	1.4	1.1	0.8	0.6	0.3	0.3	0.5	0.4	0.4	0.7
	Max.	1	13.0	10.0	16.0	31.0	21.0	26.0	24.0	12.0	21.0	15.0	9.0	9.0	31.0
Pan Evaporation(mm.)	Total	1	75.9	71.9	127.7	204.2	193.4	139.2	145.4	117.1	126.2	110.4	73.3	52.2	1436.8
Rainfall(mm)	Total	1	24.3	-	-	29.7	95.2	127.1	293.9	371.3	168.1	251.7	-	1.8	1363.1
	Num. of Days	1	1.0	-	-	3.0	13.0	20.0	24.0	27.0	24.0	18.0	-	2.0	132.0
	Daily Max.	1	24.3	-	-	25.7	23.5	16.1	52.9	95.0	37.0	128.0	-	1.7	128.0
Phenomena(Days)	Fog	1	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	17.0	18.0	41.0
	Haze	1	1.0	13.0	5.0	13.0	5.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	38.0
	Hail	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	ThunderStorm	1	1.0	0.0	0.0	3.0	4.0	a9.0	8.0	6.0	13.0	5.0	0.0	0.0	49.0
	Squall	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

B.2). Example of Meteorological Data – Rawinsonde Data

RAWINSONDE DATA

OBSERVATIONS AT STANDARD PRESSURE LEVELS

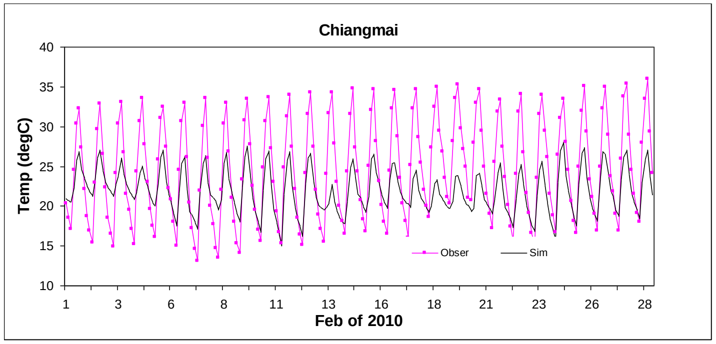
Station (327501) 48327 CHIANG MAI
MONTHLY DYNAMIC HEIGHT
JANUARY 2010 0000 GMT(0700 LST)
Latitude 18.47 N Longitude 98.59 E
Geopotential of screen 314 m.

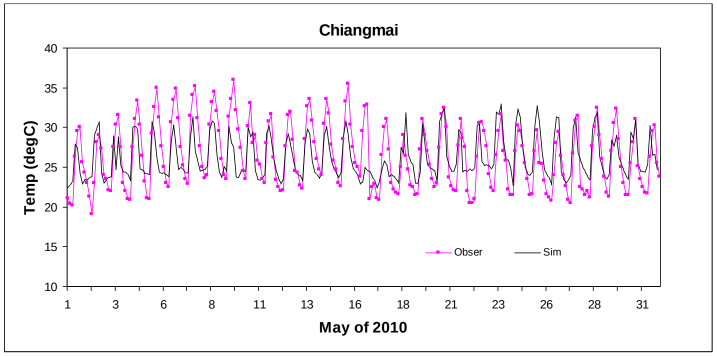
Day	STANDARD PRESSURE LEVELS (mbs)																
	1000	850	700	600	500	400	300	200	150	100	70	50	30	20	10	5	Termination
1	109	1504	3138	4396	5854	7570	9678	12415	14197	16544	18559		20248				
2	116	1510	3136	4401	5858	7593	9700	12440	14222	16567	18549	20512	23027				
3	132	1525	3151	4419	5883	7610	9712	12453	14243	16573	18576	20529	23474				
4	115	1512	3138	4403	5879	7601	9699	12434	14223	16568	18564		20172				
5	103	1501	3129	4392	5859	7582	9680	12421	14203	16560	18576	20530	23065				
6	109	1512	3143	4402	5862	7578	9684	12420	14217	16560	18571	20537	22457				
7	120	1529	3164	4423	5867	7573	9687	12435	14227	16573	18574	20531	20959				
8	140	1541	3168	4417	5854	7560	9674	12418	14206	16560	18569	20520	22693				
9	125	1527	3150	4408	5865	7568	9680	12428	14219	16562	18560	20509	23699				
10	120	1519	3144	4411	5872	7586	9705	12449	14241	16574	18563		20276				
11	124	1522	3157	4427	5878	7601	9718	12458	14254	16590	18583	20539	22444				
12	124	1527	3156	4424	5880	7595	9702	12438	14229	16577	18570	20544	24376				
13	135	1541	3170	4441	5891	7608	9709	12448	14232	16574			17387				
14	160	1563	3184	4451	5893	7604	9707	12439	14222	16584	18609	20583	23720				
15	164	1562	3190	4455	5897	7606	9697	12421	14204	16582	18604	20578	21615				
16	172	1570	3189	4449	5902	7613	9701	12420	14207	16587	18608	20577	21516				

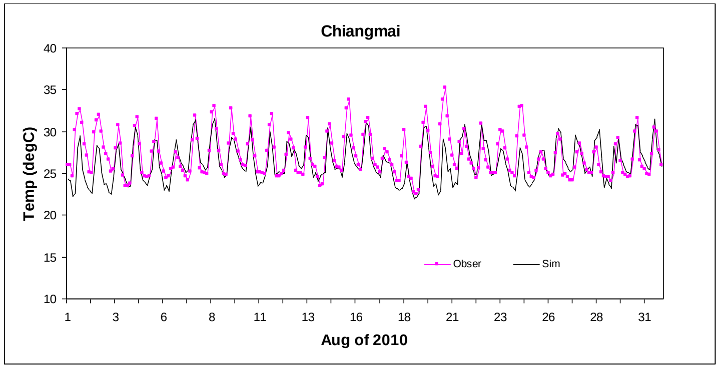
Day	STANDARD PRESSURE LEVELS (mbs)																
	1000	850	700	600	500	400	300	200	150	100	70	50	30	20	10	5	Termination
17	174	1571	3183	4448	5904	7616	9702	12418	14205	16574	18604	20584	21447				
18	168	1563	3177	4440	5902	7609	9704	12422	14213	16574	18619	20594	21092				
19	153	1545	3163	4432	5887	7593	9685	12412	14194	16558	18594		20376				
20	151	1547	3169	4430	5880	7587	9679	12404	14202	16566	18609	20578	22867				
21	131	1533	3160	4420	5867	7576	9672	12400	14193	16560	18588		19975				
22	128	1531	3159	4417	5860	7562	9660	12388	14184	16549	18573	20555	22694				
23	135	1541	3166	4418	5865	7561	9641	12377	14172	16549	18587	20556	21111				
24	136	1544	3172	4425	5858	7551	9624	12366	14157	16548	18585	20551	23130				
25	143	1547	3173	4426	5866	7557	9630	12358	14156	16537	18573	20537	23504				
26	137	1538	3165	4412	5851	7536	9611	12348	14140	16512			17505				
27	142	1546	3168	4417	5846	7535	9608	12344	14132	16522	18566		19409				
28	138	1540	3159	4427	5866	7576	9666	12387	14166				14282				
29	140	1540	3162	4417	5871	7585	9673	12398	14166	16564	18577		19943				
30	141	1536	3159	4417	5866	7579	9673	12388	14180	16561			17716				
31	139	1540	3163	4419	5869	7569	9662	12385					12665				
N	31	31	31	31	31	31	31	31	30	29	26	19	31				
Mean	136	1536	3161	4422	5873	7582	9678	12411	14200	16562	18581		20930				
Max.	174	1571	3190	4455	5904	7616	9718	12458	14254	16590	18619	20594	24376				
Min.	103	1501	3129	4392	5846	7535	9608	12344	14132	16512	18549	20509	12665				

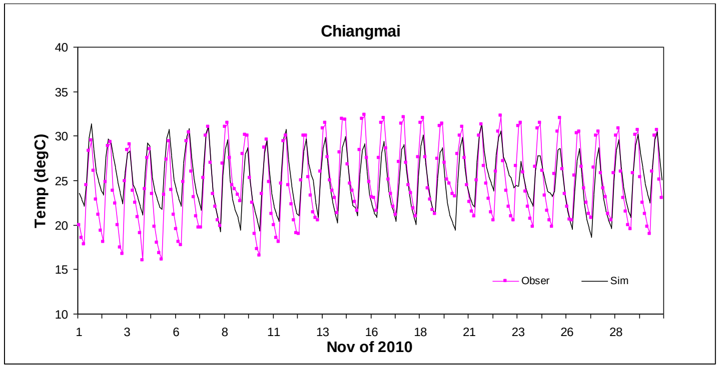
B.3). Diurnal Trends of Observation and Simulation Data

3 Hourly In-Pair Comparisons of Ground (2 meter) Temperature in Chiangmai Station

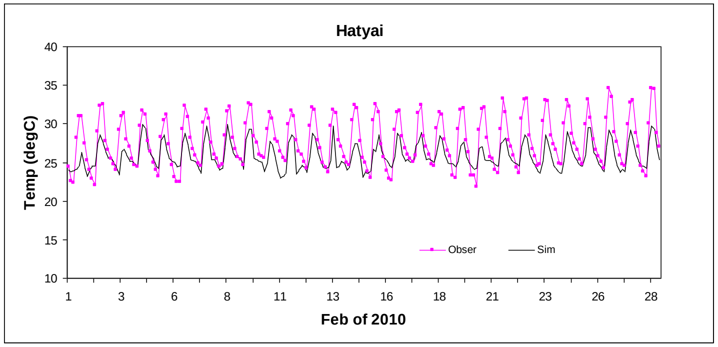


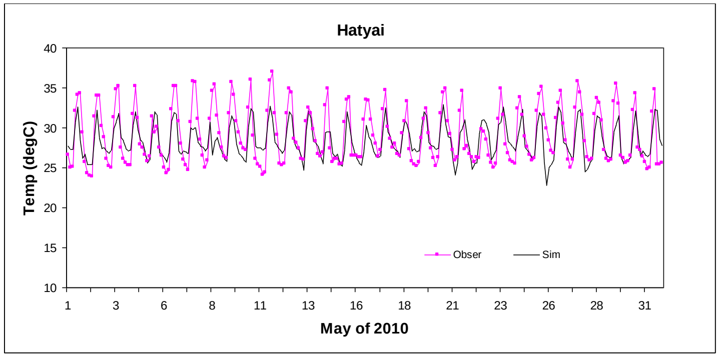


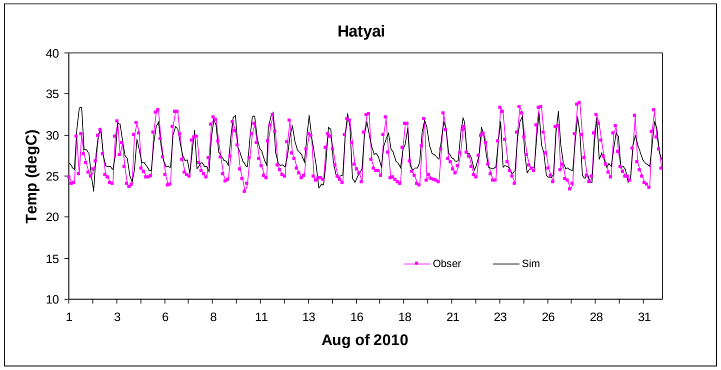


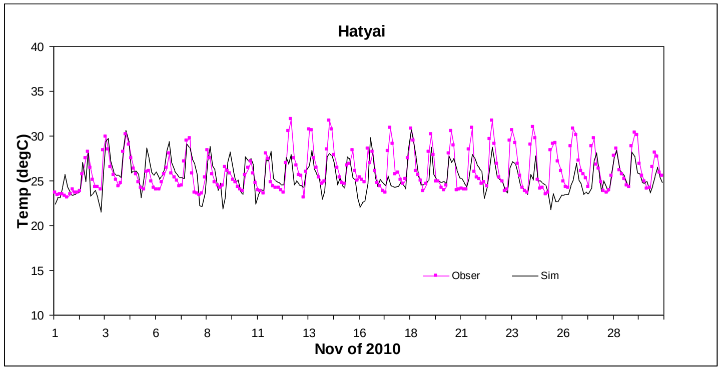


3 Hourly In-Pair Comparisons of Ground (2 meter) Temperature in Hatyai Station

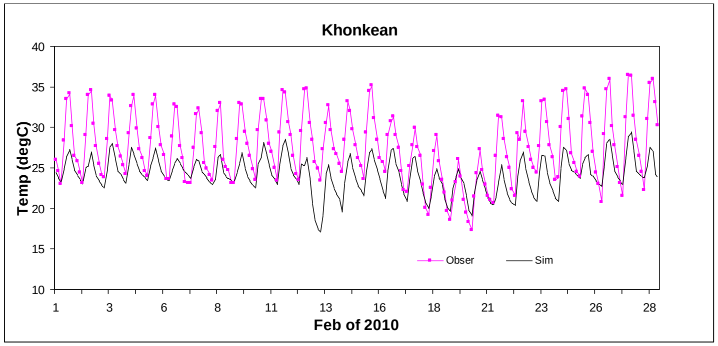


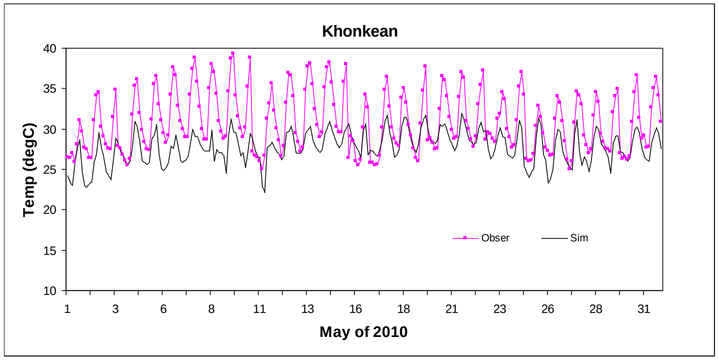


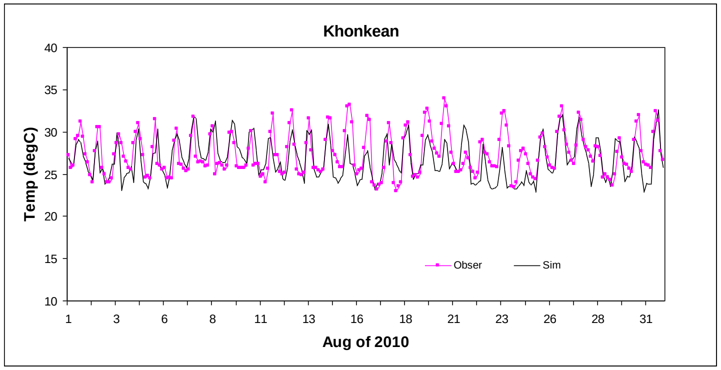


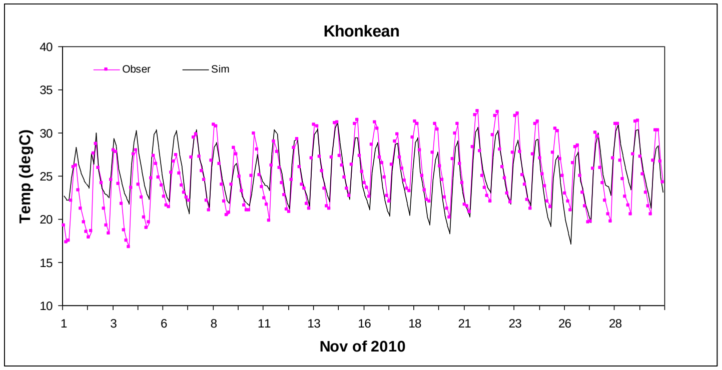


3 Hourly In-Pair Comparisons of Ground (2 meter) Temperature in KhonKaen Station

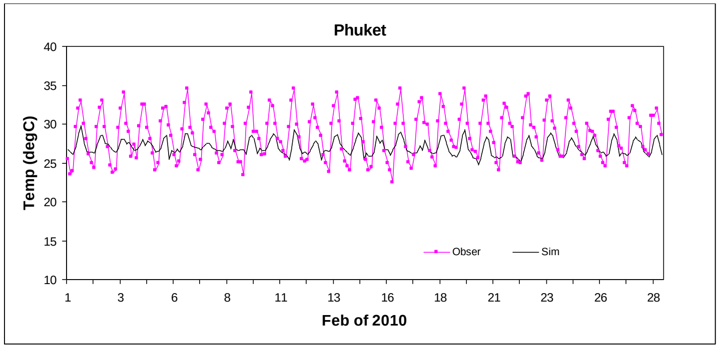


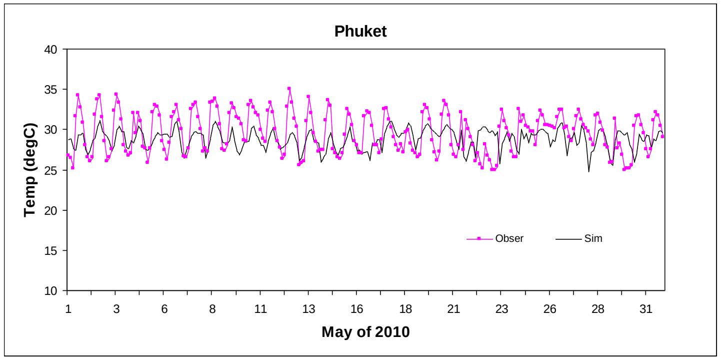


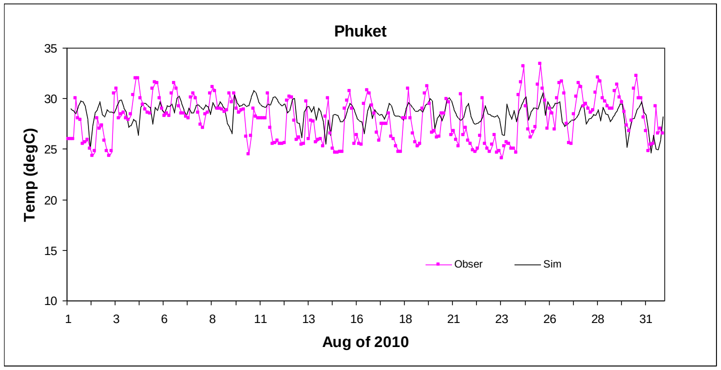


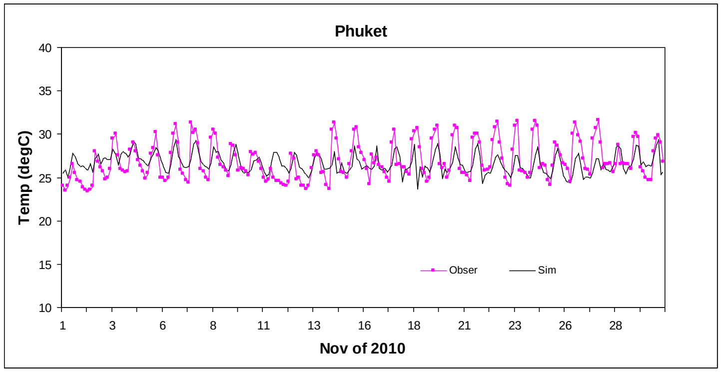


3 Hourly In-Pair Comparisons of Ground (2 meter) Temperature in Phuket Station

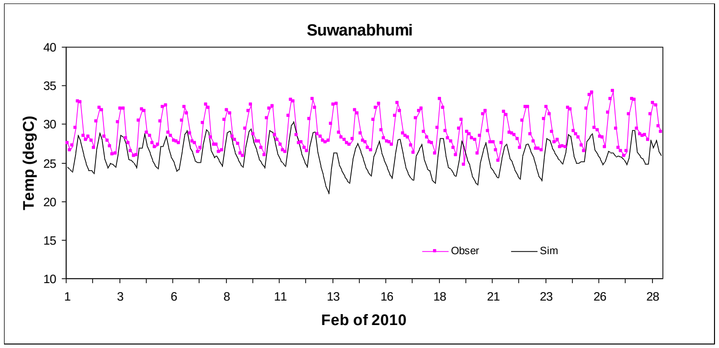


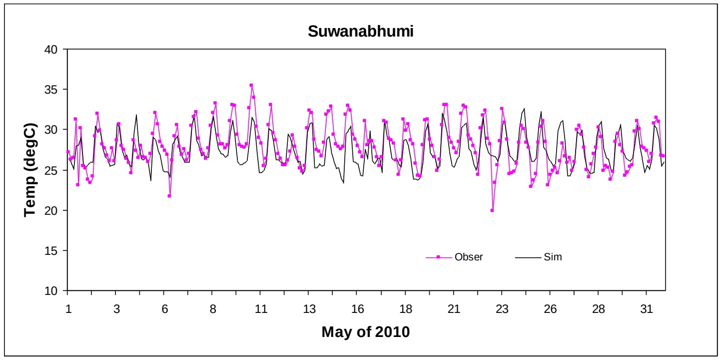


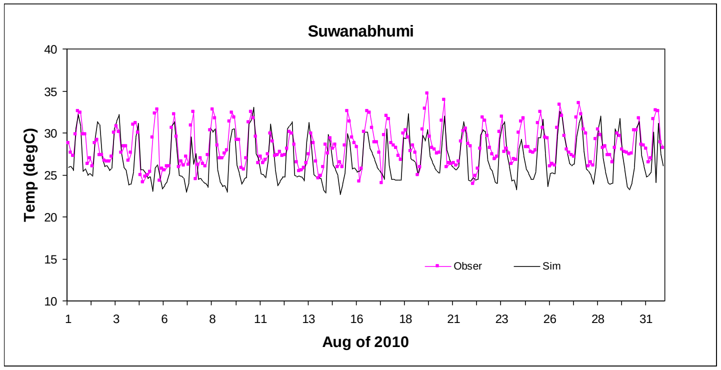


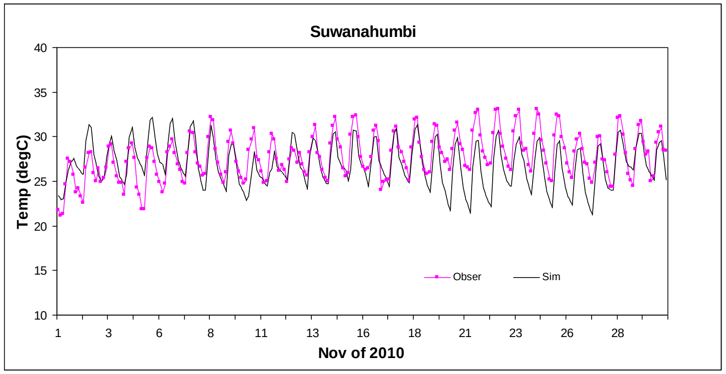


3 Hourly In-Pair Comparisons of Ground (2 meter) Temperature in Suwanabhumi Station

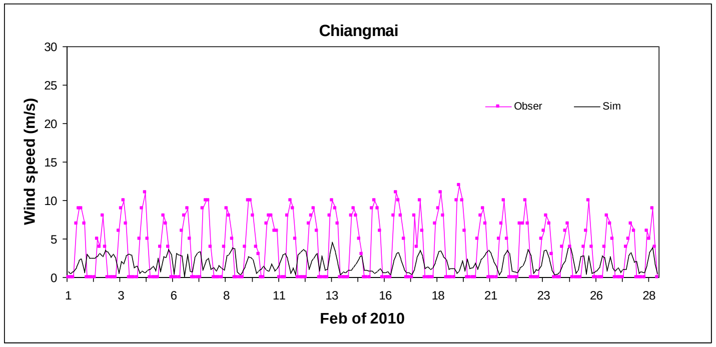


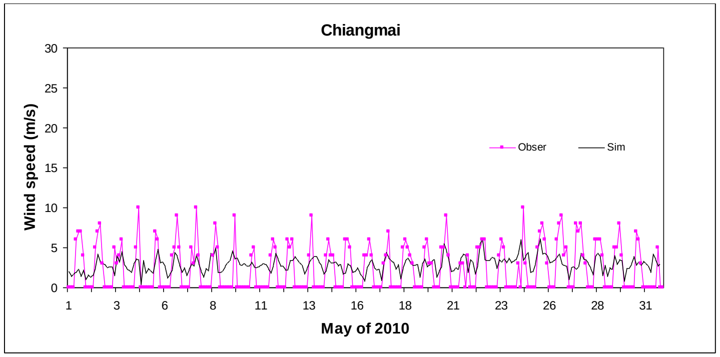


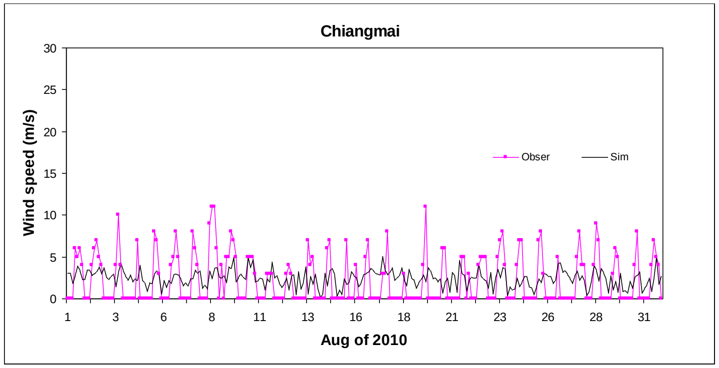


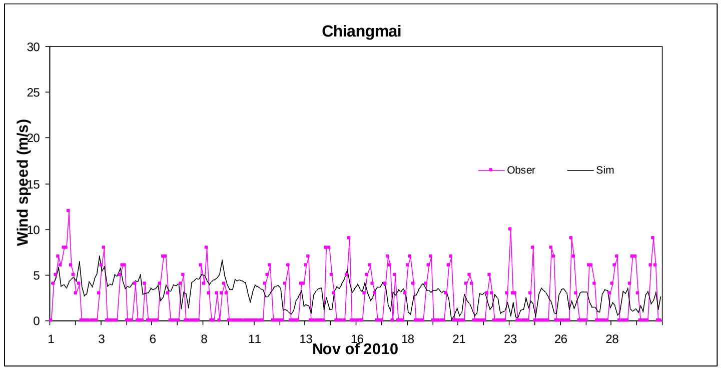


3 Hourly Pair Comparisons of Wind Speed in Chiangmai Station

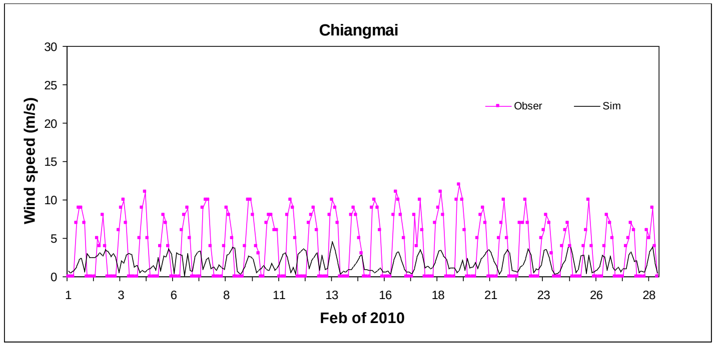


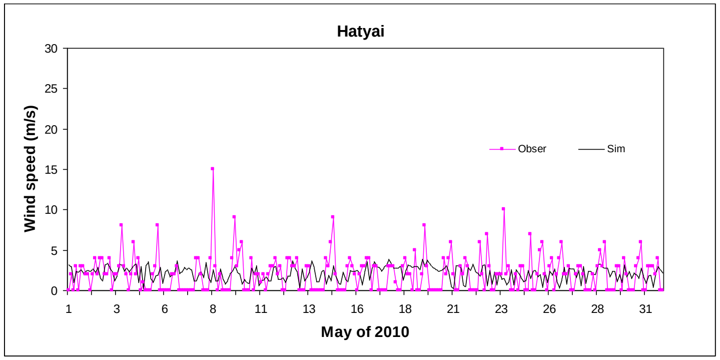


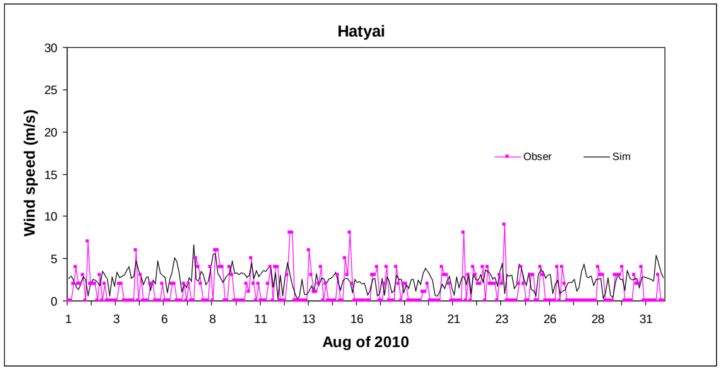


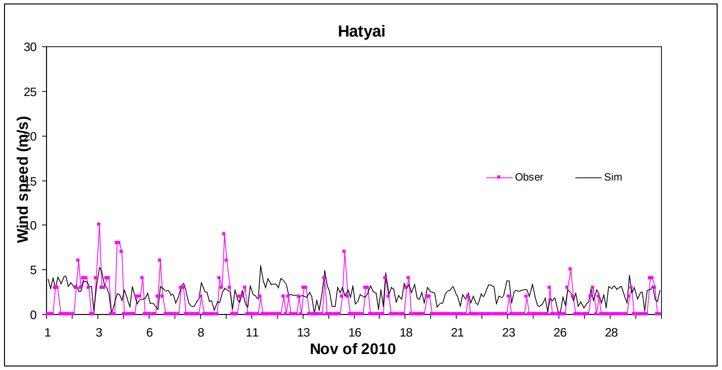


3 Hourly Pair Comparisons of Wind Speed in Hatyai Station

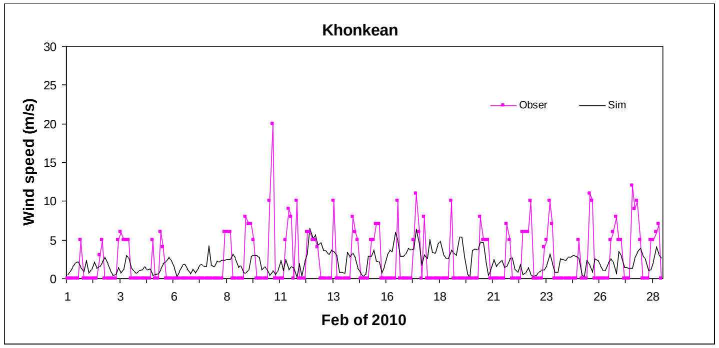


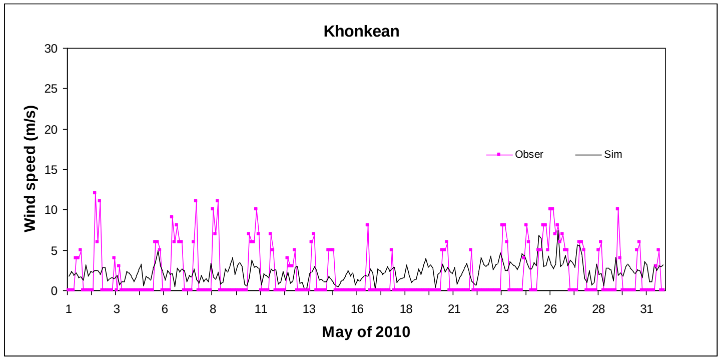


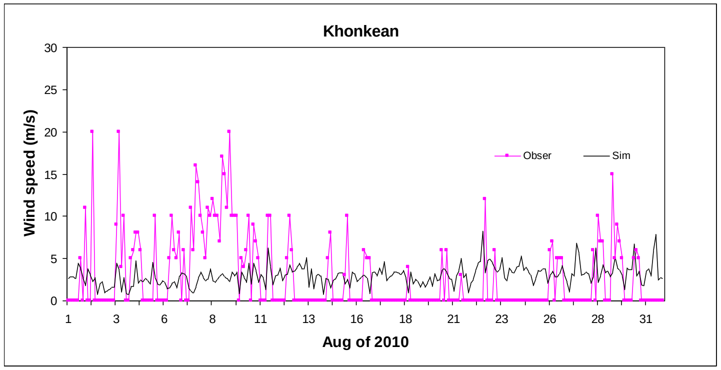


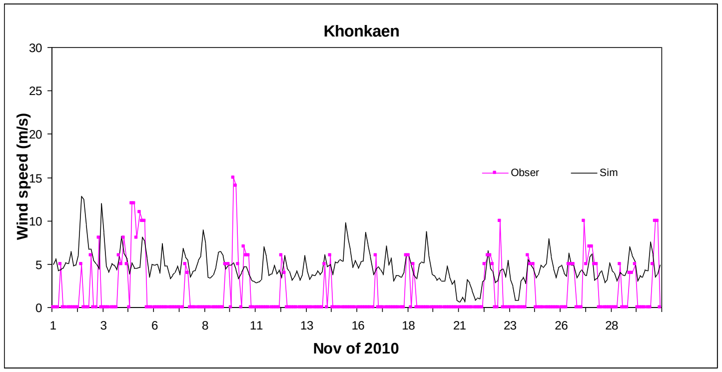


3 Hourly Pair Comparisons of Wind Speed in KhonKaen Station

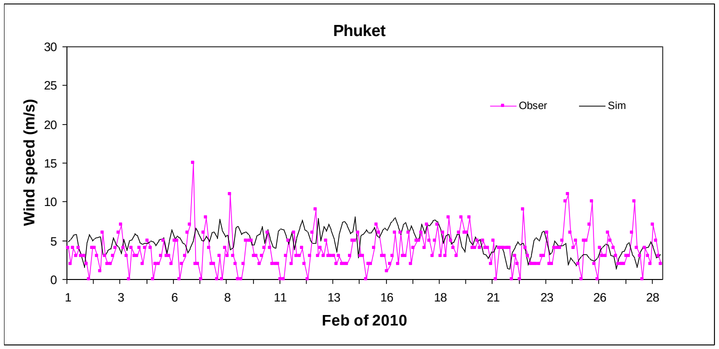


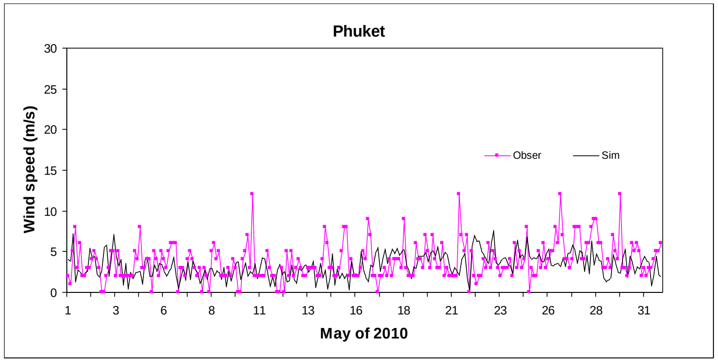


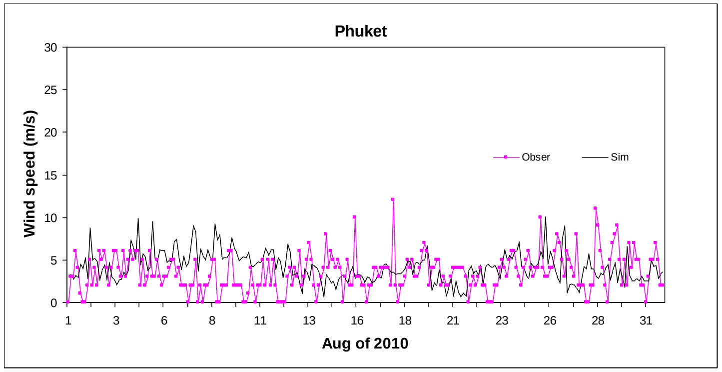


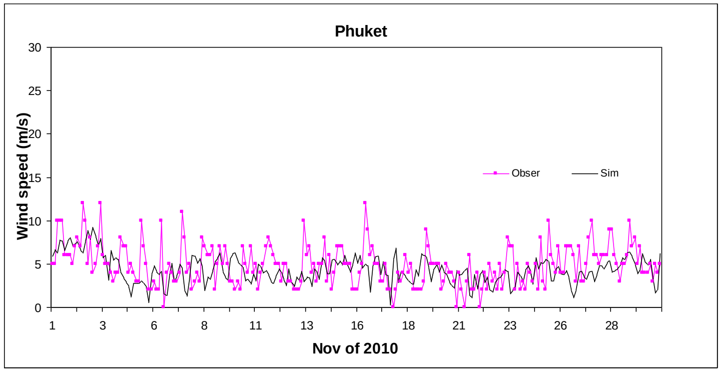


3 Hourly Pair Comparisons of Wind Speed in Phuket Station

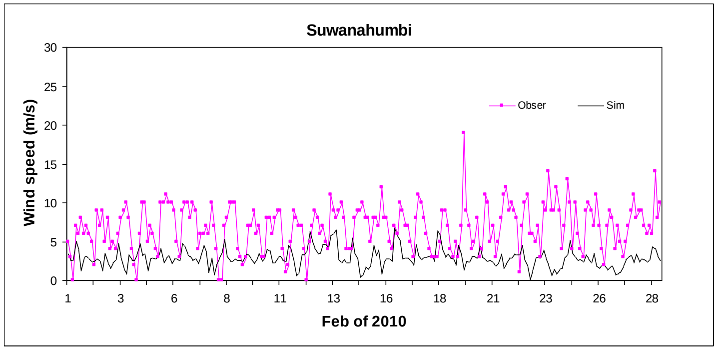


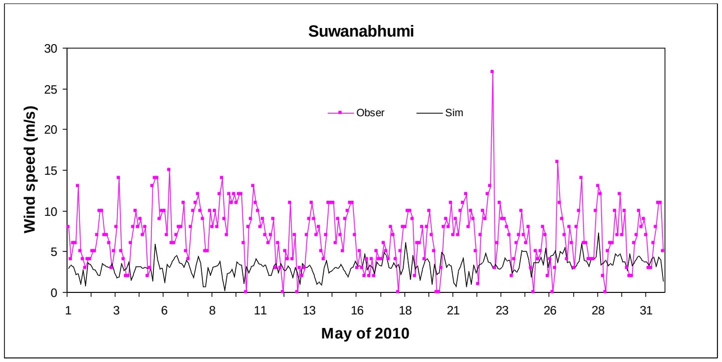


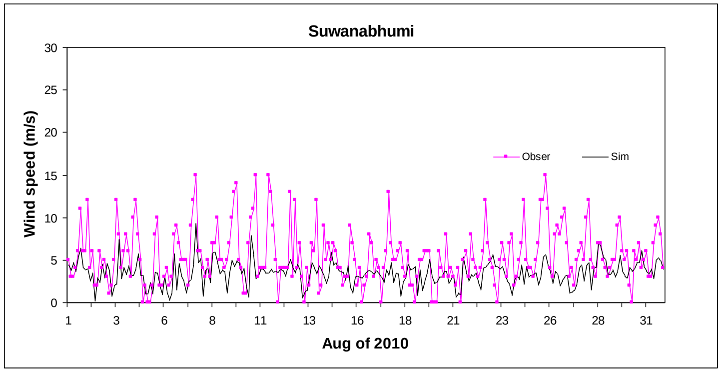


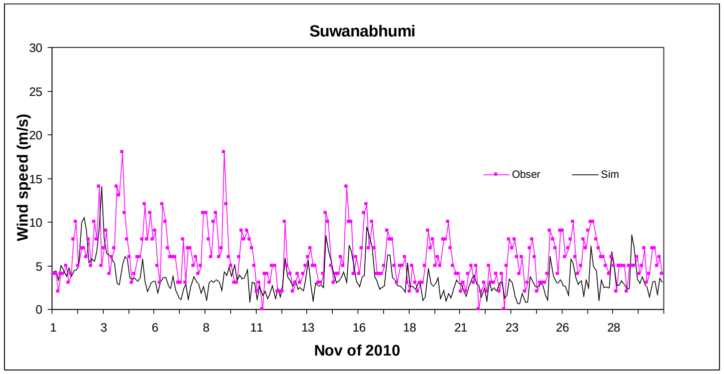


3 Hourly Pair Comparisons of Wind Speed in Suwanabhumi Station

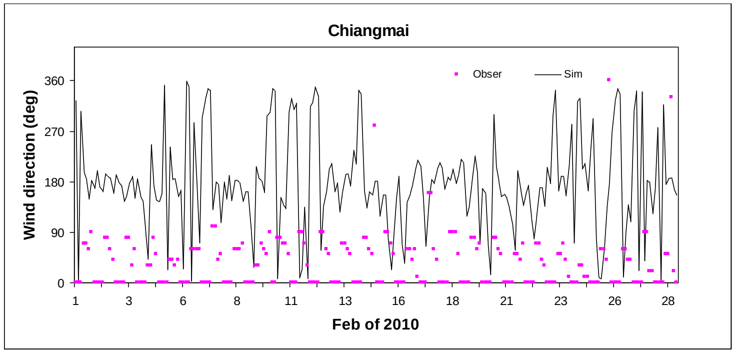


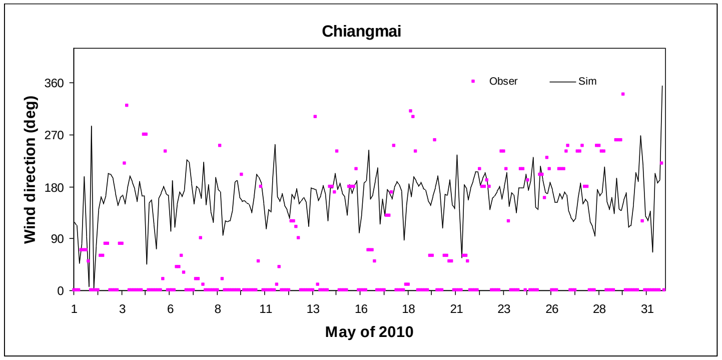


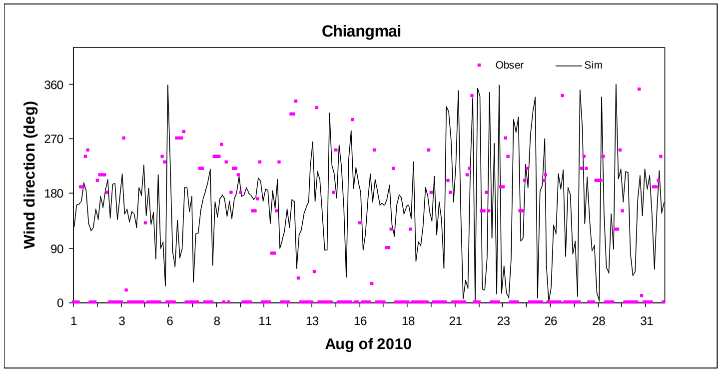


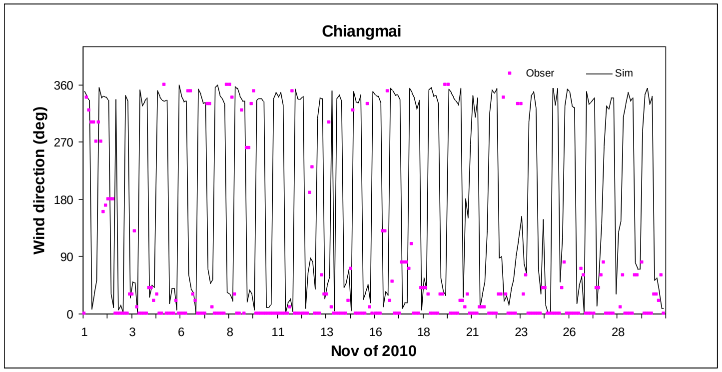


3 Hourly Pair Comparisons of Wind Direction in Chiangmai Station

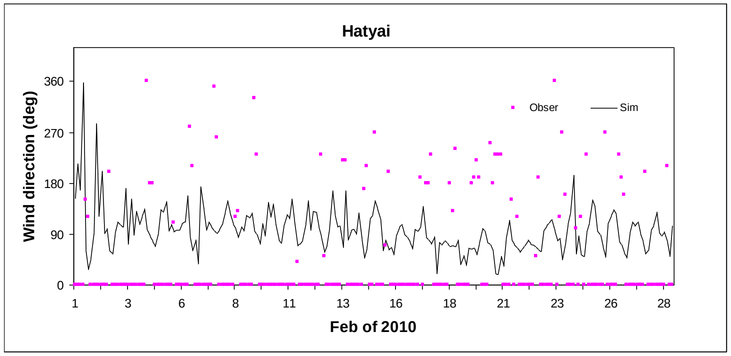


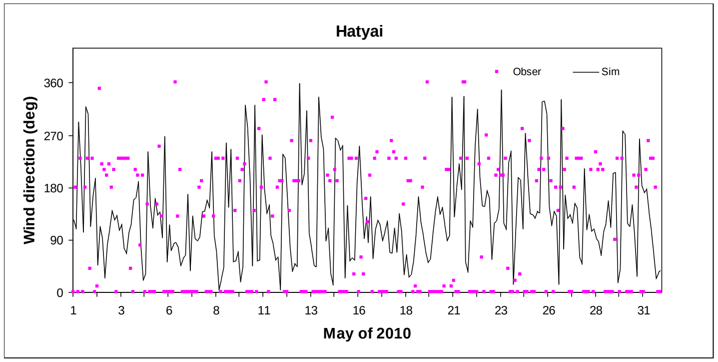


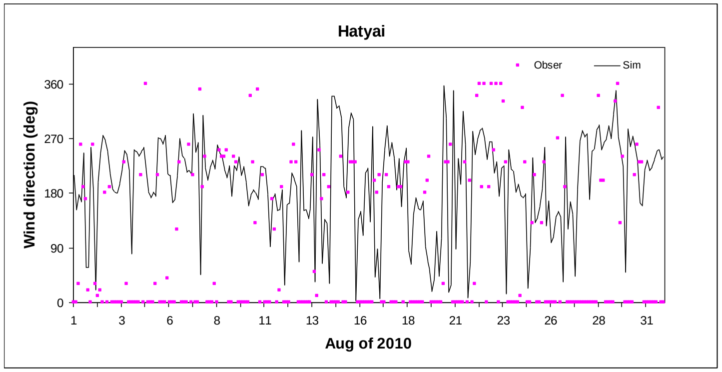


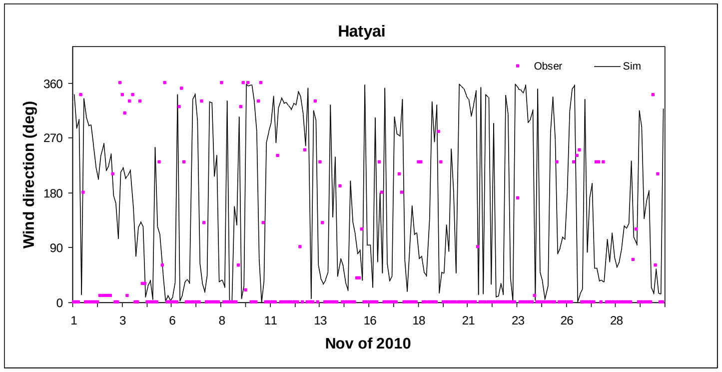


3 Hourly Pair Comparisons of Wind Direction in Hatyai Station

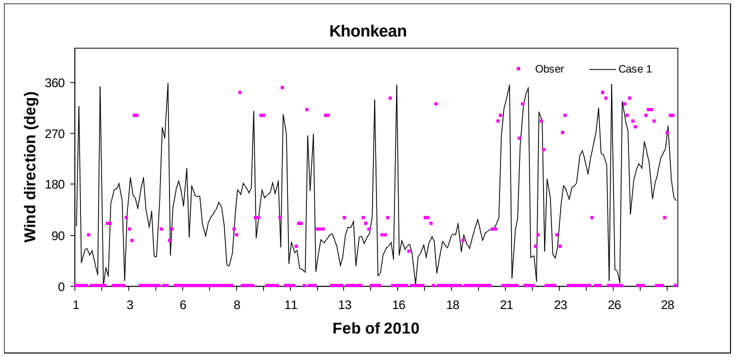


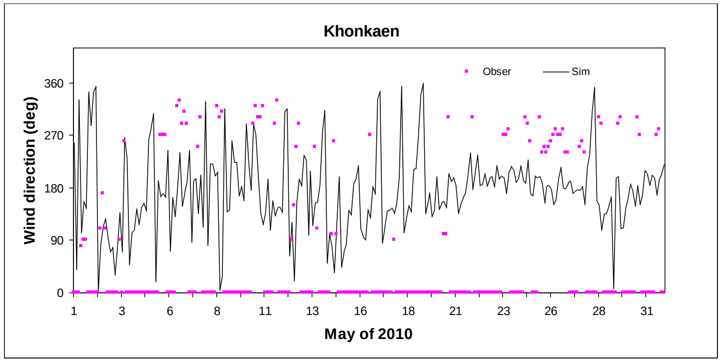


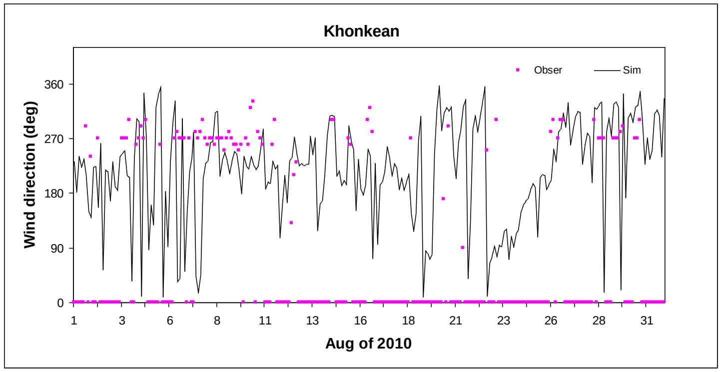


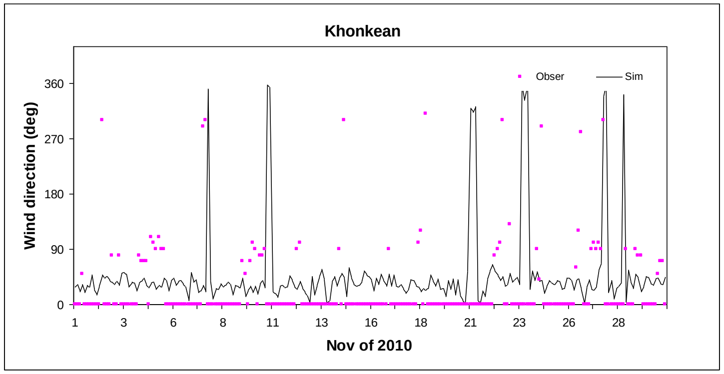


3 Hourly Pair Comparisons of Wind Direction in KhonKean Station

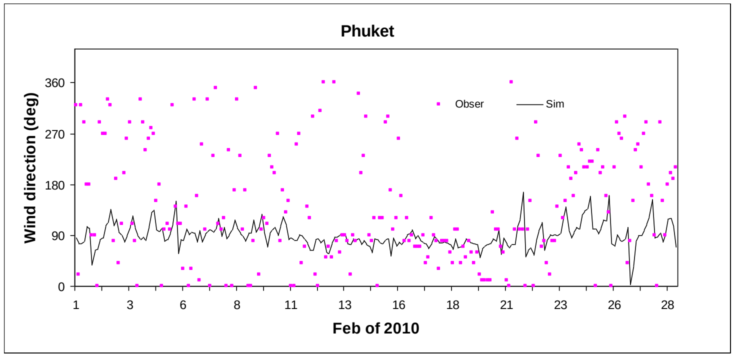


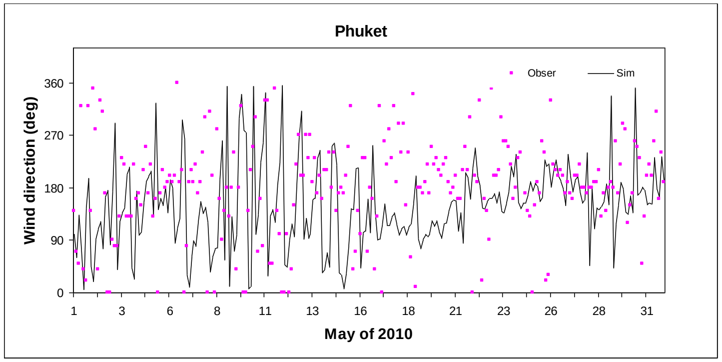


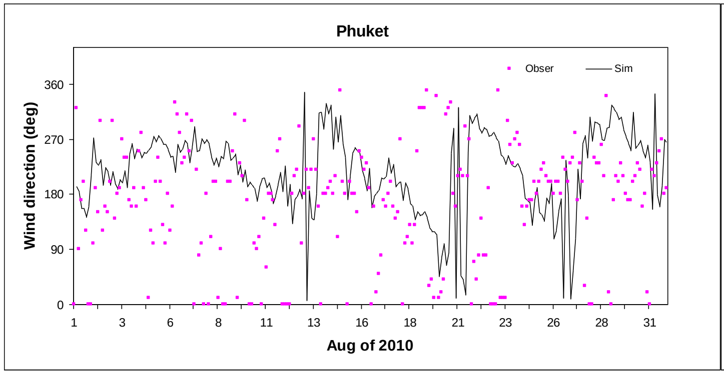


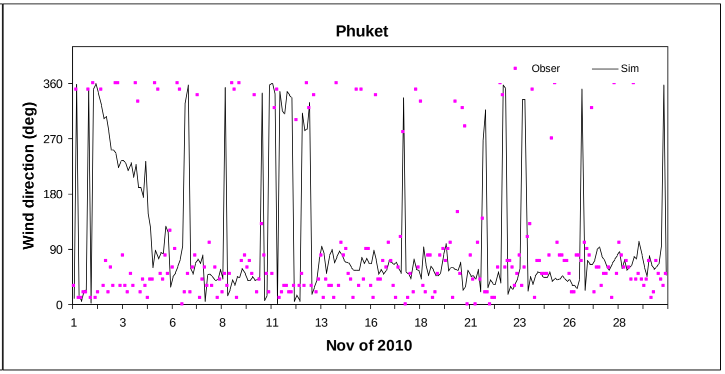


3 Hourly Pair Comparisons of Wind Direction in Phuket Station

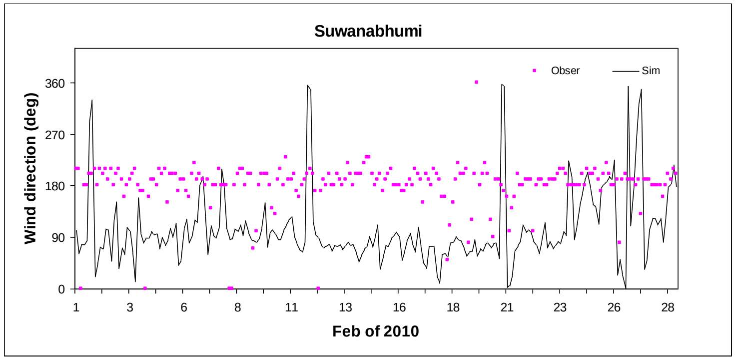


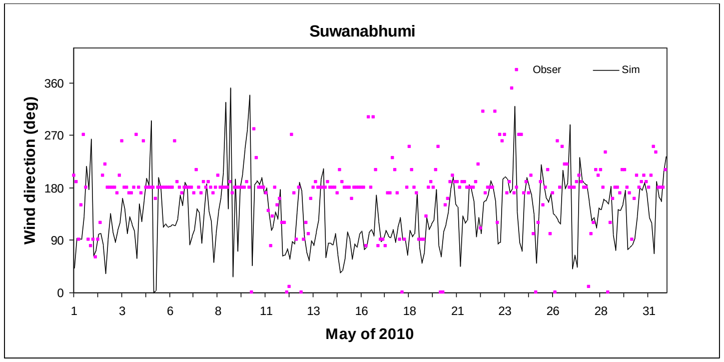


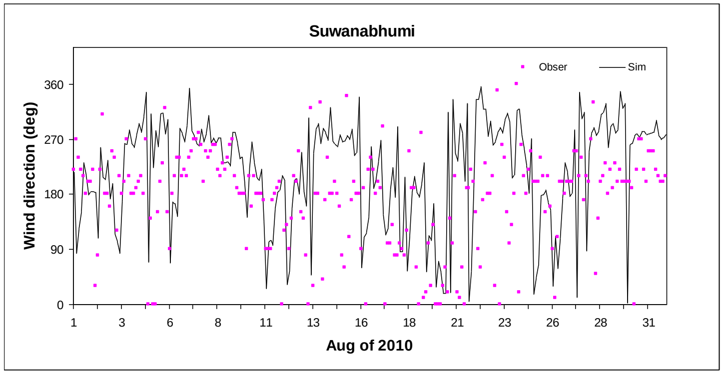


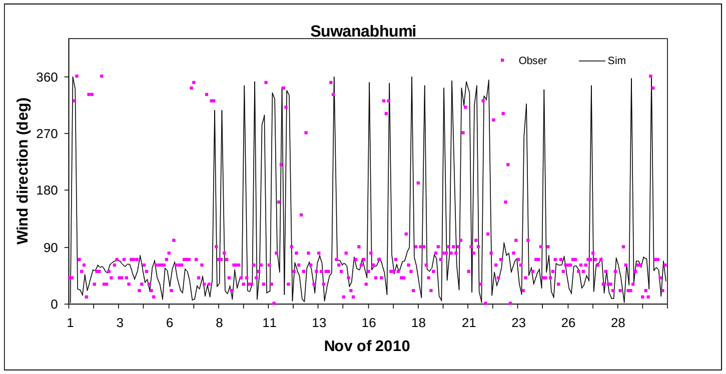


3 Hourly Pair Comparisons of Wind Direction in Suwanabhumi Station

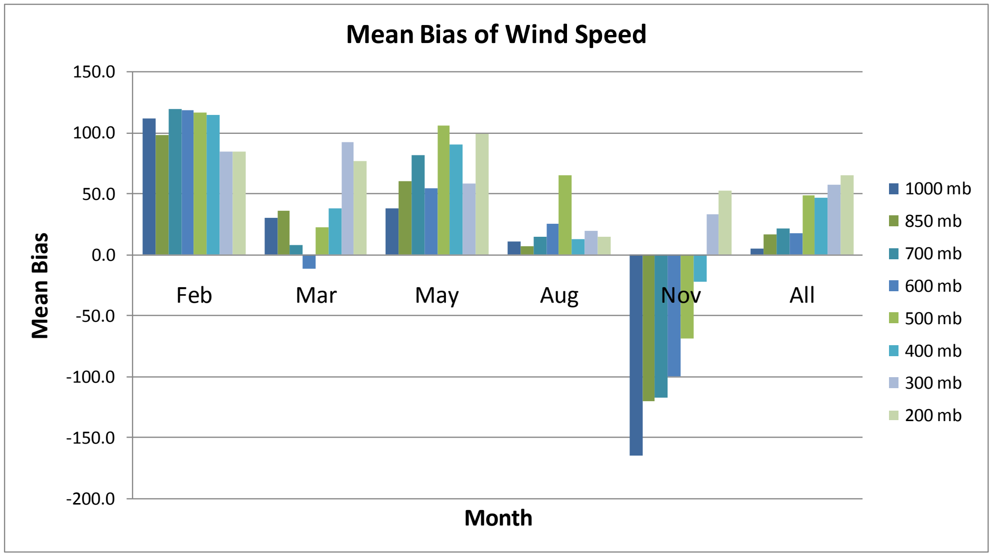








Mean Bias of Wind Speed from Sounding Data



APPENDIX C

INFORMATION RELATED TO AN INVESTIGATION OF AIR QUALITY MODEL

C.1). Example of Air Quality Ambient Data

C.2). Diurnal Trends of Observation and Simulation

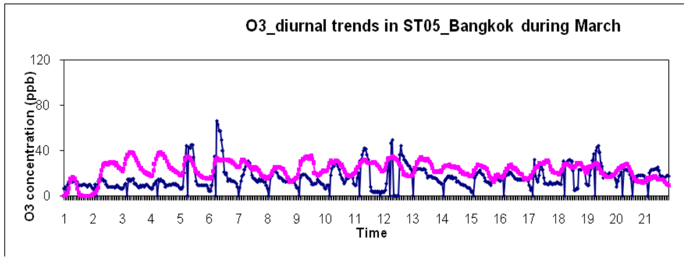
C.1). Example of Air Quality Ambient Data

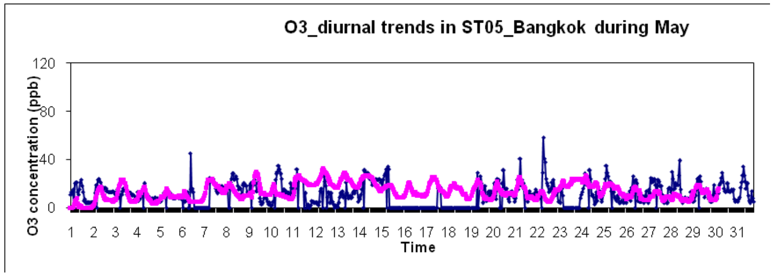
Station Chiangmai (36T)

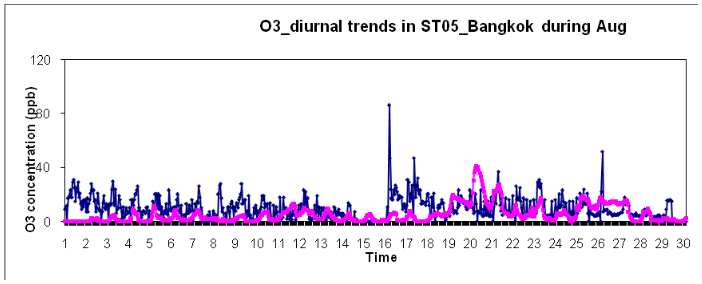
Year (2digit) Month (2digit) Day (2digit)	Hour	CO	NO	NOX	NO2	SO2	O3	PM10
		at 3 m (ppm)	at 3 m (ppb)	at 3 m (ppb)	at 3 m (ppb)	at 3 m (ppb)	at 3 m (ppb)	at 3 m (มคก./ลบ.ม.)
100101	100	0.7	25	46	21	1	2	84
100101	200	0.8	19	38	19	0	1	54
100101	300	0.5	17	33	16	0	1	32
100101	400	0.5	13	30	17	0	0	37
100101	500	0.6	15	29	14	0	0	40
100101	600	0.8	28	41	13	0	0	46
100101	700	0.7	31	42	11	0	0	37
100101	800	0.7	35	47	12	0	1	46
100101	900	0.3	19	31	12	0	5	43
100101	1000	0	7	14	7	0	14	26
100101	1100	0	5	11	6	0	26	25
100101	1200	0.1	4	13	9	0	37	29
100101	1300	0	3	11	8	0	44	15
100101	1400	0	4	12	8	0	42	14
100101	1500	0	5	10	6	0	35	16
100101	1600	0	4	11	7	0	34	14
100101	1700	0.2	6	19	13	0	34	41
100101	1800	0.9	16	46	30	0	12	54
100101	1900	-	-	-	-	-	-	35
100101	2000	1.9	63	97	34	1	1	54
100101	2100	2.2	74	108	34	2	1	98
100101	2200	0.9	17	46	29	0	1	50
100101	2300	1.1	29	59	30	0	1	66
100101	2400	0.5	9	29	20	0	2	30

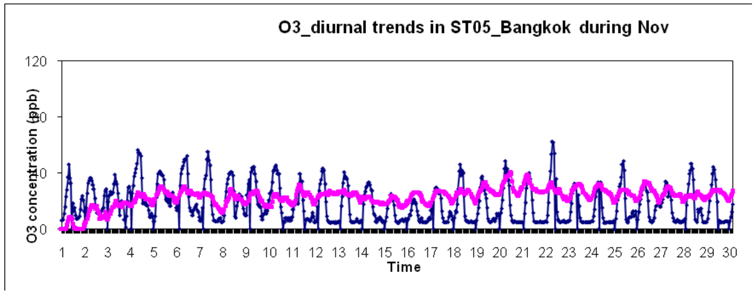
C.2). Diurnal Trends of Observation and Simulation

Hourly Pair Comparisons of O3 Ambient Concentration Station Bangkok ST05

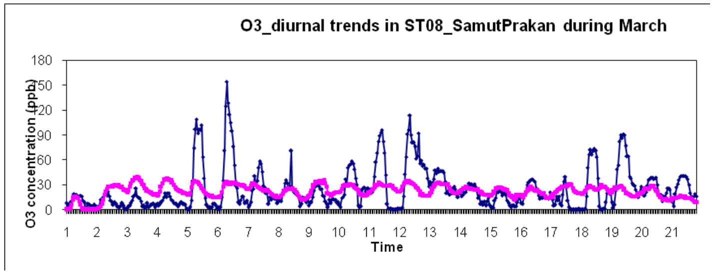


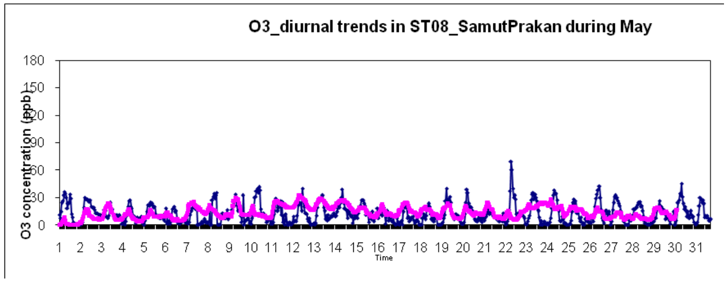


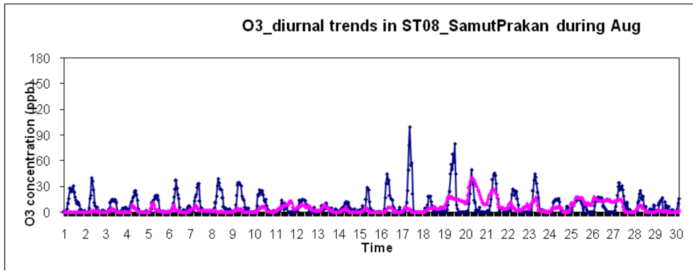


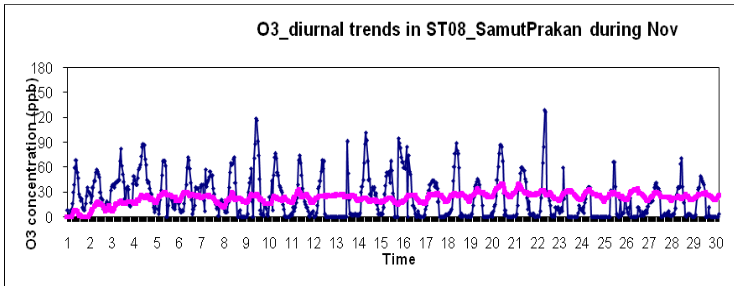


Hourly Pair Comparisons of O3 Ambient Concentration Station Samutprakan ST08

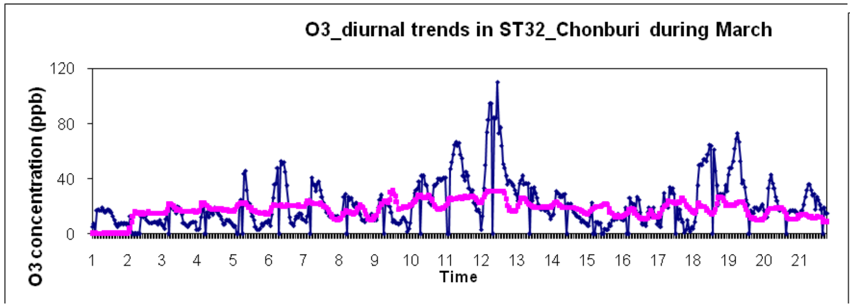


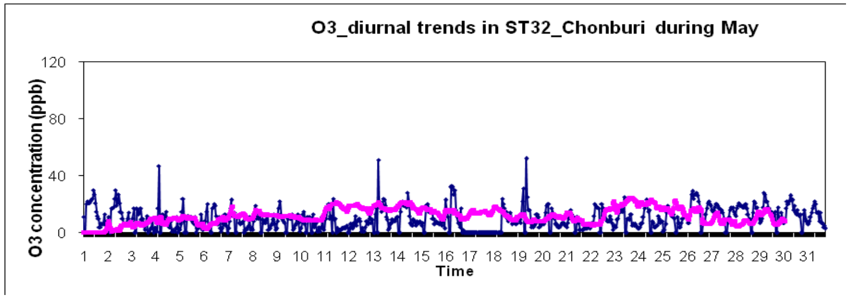


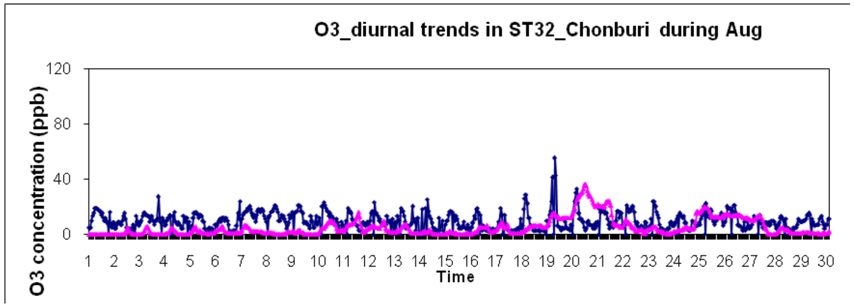


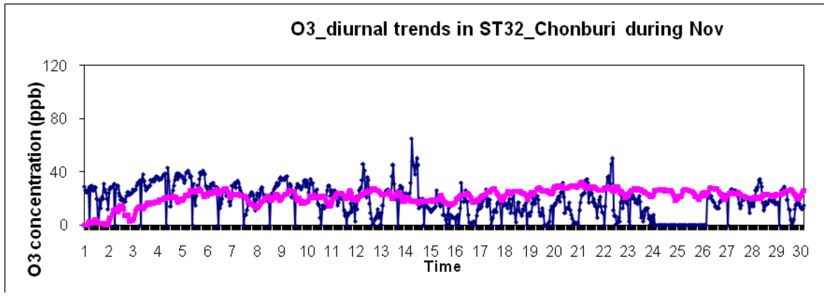


Hourly Pair Comparisons of O3 Ambient Concentration Station Chonburi ST32

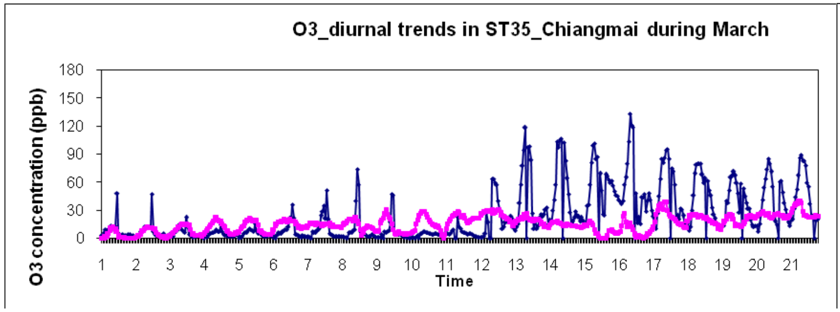


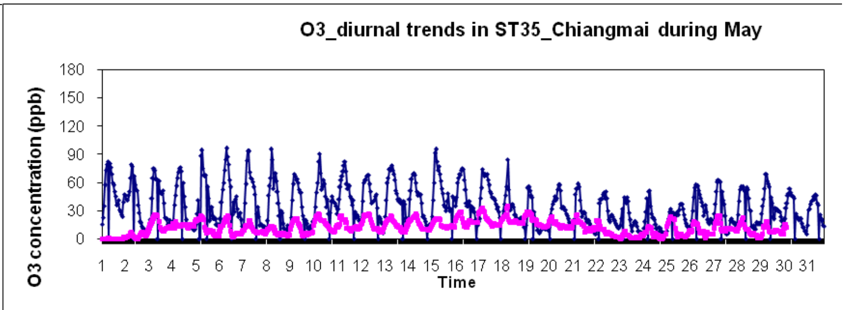


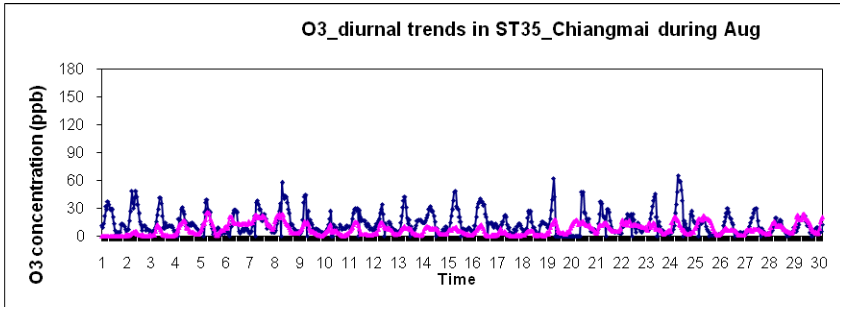


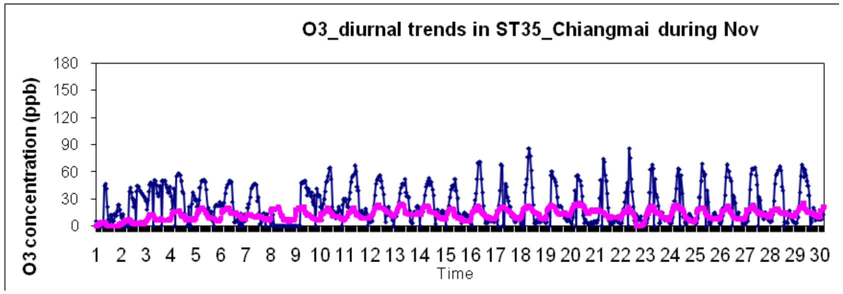


Hourly Pair Comparisons of O3 Ambient Concentration Station Chiangmai ST35


O3_diurnal trends in ST35_Chiangmai during March


O3_diurnal trends in ST35_Chiangmai during May


O3_diurnal trends in ST35_Chiangmai during Aug


O3_diurnal trends in ST35_Chiangmai during Nov