Generation of Volatile Organic Compounds (VOCs), Oxides of Nitrogen (NOx), and Ozone (O3) during Smog Case Study: Chiang Rai Province

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Abstract

Pollution from human activities affects livelihood, quality of life and environment of communities. So goals of this research study on pollution concentration of Volatile Organic Compounds (VOCs), oxides of Nitrogen (NO_x), and Ozone (O_3) in Chiang Rai Province was monitored in two periods; before the forest burning during November 13-15, 2015 in winter, and during the forest burning during March 23-17, 2016 in summer. The monitoring was conducted at Ban San Kong School by using ambient air quality monitoring mobile unit with sampling equipment as follows: Gas chromatograph/flame ionization (GC/FID), NO_x analyzer, and Ozone analyzer.

The results revealed that the concentration of VOCs and NO_x related to the source. VOCs in other VOCs group (Freon-12, acetylene, vinyl chloride, chloroform, CCl_4) were detected in the highest concentration which was generated from anthropogenic sources. The sources of the concentration of NO_x were fuel combustion and traffic. Meanwhile, the concentration of O_3 was the product of the secondary reaction between VOCs and NO_x, therefore, the higher concentration of NO_x resulted in a higher concentration of O_3.

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The comparison of VOCs, NO_x and O_3 concentration between before and during the forest burning indicated that the concentration of NO_x and O_3 are high whereas the concentration of VOCs is low because VOCs are oxidized to their radicals and react with NO_x in the atmosphere and produce O_3.

Keywords: Volatile organic compounds, Ozone, Oxides of Nitrogen and Chiang Rai

INTRODUCTION

Air pollution is a severe problem with broad impacts. A significant worldwide pollutant released directly from sources is nitrogen oxide because it introduces acid rain and photochemical smog that weakens the human respiratory system. The expansion of urban areas, economic and industry development accelerates the deterioration and toxicity of the environment (Rungratanaubon et al, 2018). Smog problems in the north of Thailand occur every year in the dry season (December to April). It impacts on the respiratory system of human especially those with a weak immune system. In addition, the smog also effects tourism and obstructs visibility which impacts on traffic system.

The severity of the problem is reinforced by three conditions which are the basin and range topography, the temperature variation between the peak and foothill where are the human residences and human activities including traffic, brick production, construction, post-harvest burning, waste burning, and forest fire. These activities generate particulate matter, volatile organic compounds, oxides of nitrogen, ozone, and carbon monoxide etc. in the atmosphere. When the higher temperature of the air at the foothill vertically floats to the atmosphere and expands until its temperature is equal to the surrounding which is lower and it is unable to disperse, the accumulation of pollutants takes place. More burning causes a higher concentration of pollutants. In the atmosphere, the photochemical reaction of a pollutant occurs when nitric oxide gas (NO) is oxidized to nitrogen dioxide gas (NO_2).

The oxidation reaction in the atmosphere is accelerated with the occurrence of hydrocarbon compounds (HC) (Teeta, 2008). At normal temperature conditions, the reaction rate increases when the concentration of nitric oxide gas (NO) and oxygen gas (O2) (Williamson, 1973) increases. Nitrogen dioxide (NO_2) in the atmosphere is reduced by ultraviolet radiation to be NO and oxygen atoms (O), and Ozone (O_3)

reacts with NO to generate NO_2 and O_2. According to the reaction equation, higher NO_2 concentration results in an increase of O_3. On the other hand, higher NO concentration results in a decrease of O_3. After that, oxygen atoms (O) and O_3 react with volatile organic compounds (VOCs) comprising non-methane hydrocarbons (NMHC), methane (CH4), aldehydes, and carbon monoxide (CO) to generate free radicals etc. (Akimoto et al, 1994). NO_2 generated from the above equations is the reactant of photochemical reactions to produce O_3. Meanwhile, the remaining NO_2 reacts with free radicals to generate the oxidants in the following steps; The photochemical reaction changes the proportion of pollutants in the atmosphere and can strengthen or weaken of their toxicity depending on types of pollutants in the atmosphere.

OBJECTIVES OF THE STUDY

1. Investigate the concentration of Volatile Organic Compounds (VOCs), Oxide of Nitrogen (NO_x), and Ozone (O_3) in two periods; before the forest burning and during the forest burning.

2. Study the relationship of Volatile Organic Compounds (VOCs), Oxides of Nitrogen (NO_x), and Ozone (O_3) before and during the forest burning period.

MATERIALS AND METHODS

Sampling Method

The samples were collected in two periods; before the forest burning during November 13-15, 2015 in winter, and during the forest burning during March 23-17, 2016 in summer at Ban San Kong School, Chiang Rai Province (Figure 1.). The results were compared and analyzed for the trend in a day.

Equipment

Meteorological Condition Monitoring

The Ambient Air Quality Monitoring Mobile Unit collected four parameters of meteorological conditions at 10 meters above ground. The monitored parameters were wind speed (m/s) measured by the anemometer, wind direction (0-360 degree) measured by wind vane, temperature (^{o}C) measured by temperature measuring equipment, and relative moisture (%). The equipment was installed and managed by Petro Instrument Company Limited. The equipment was operated for 24 hours per day (Figure 2).

Volatile Organic Compounds (VOCs) Monitoring

Gas chromatograph (GC) model Chromatotec was applied for VOCs monitoring. This equipment can separate each component of compounds in the sample prior feed such component into the de-

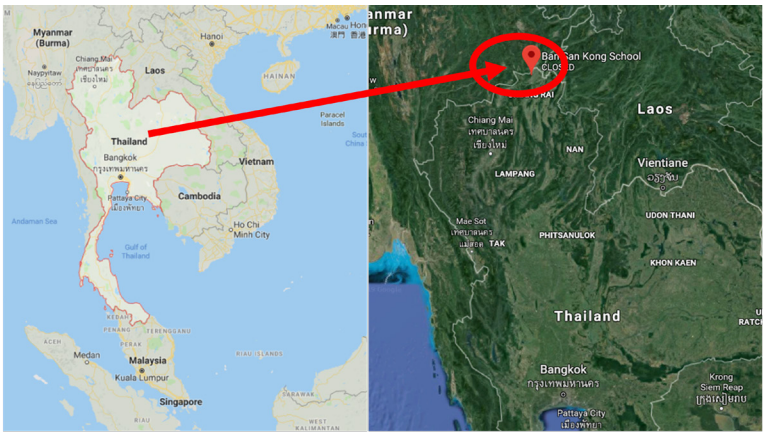


Figure 1 The area sampled at Ban San Kong School, Chiang Rai Province.

(a) (b) (c)

Figure 2 Meteorological Condition Monitoring Equipment (a) Ambient Air Quality Monitoring Mobile Unit (b) Anemometer and Wind Vane (c) Humidity-Temperature Sensor

tector to examine its mass number and amount. The VOCs monitoring equipment consists of four compartments which are Hydroxychrom, airmoCAL, airmoVOC C2-C6 (Gas analyzer, GC866 model A11000) using thermoelectric cooling to control the temperature of the sample, and airmoVOC C6-C12 (Gas analyzer, GC866 model A21022). The monitoring takes 30 minutes for each cycle. VistaCHROM 1.4.7 software is required for the analysis (Figure 3).

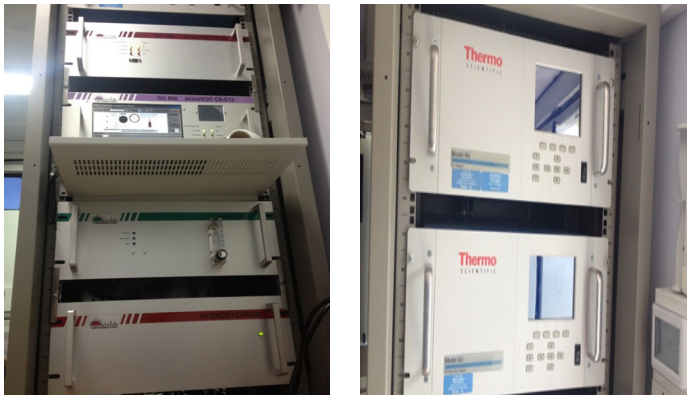
Oxides of Nitrogen Monitoring

NO_x Analyzer model 41i was applied for monitoring the concentration of oxides of nitrogen in ambient air using Chemiluminescence method. The analyzer measures the amount of oxide of nitrogen (NO_x) and nitric oxide gas (NO) then subtracts the amount of NO with the amount of NO_x to obtain the amount of nitrogen dioxide (NO_2). NO is firstly measured by using a photomultiplier tube to detect photon energy releasing from the

return of NO_2 in the electronically-excited state (NO*), generated from the reaction between NO and O_2 ($NO+O_2 \rightarrow NO_2$) to the ground state. The released photon energy is directly variation to the amount of NO. The amount of NO_x is measured by converting all oxides of nitrogen to NO and detects the total amount of NO which is equal to the total amount of NO_x. The electrical circuit in the analyzer will then calculate the amount of NO_2 by subtracting the amount of NO from the amount of NO_x. The NO_x Analyzer was operated for 24 hours per day and reported the results every hour. The readings of the Analyzer of NO_x in ambient air are presented in Figure 3.

Ozone Monitoring

Ozone analyzer model 49i was applied for monitoring the concentration of ozone in ambient air by detecting the ultraviolet (UV) absorption of the ozone molecule when path length, concentration, and wavelength of UV are constant. The relation between the concentration of O_3 and UV is corresponding to Beer-Lambert Law; the higher concentration of O_3 in the sample results in the higher absorption of UV, on the other hand, the lower concentration of O_3 in the sample results in the lower absorption of UV. The ozone Analyzer was operated for 24 hours per day and reported the results every hour. The Analyzer of NO_x in ambient air is presented in Figure 3.



(a) (b)

Figure 3 (a) Gas chromatograph (GC) (b) top: NOx Analyzer, bottom: Ozone analyzer

RESULTS AND DISCUSSION

Volatile Organic Compounds (VOCs)

Volatile Organic Compounds were classified as five groups which are alkanes, alkenes, cycloalkanes, other VOCs, and aromatics. Other VOCs had the highest concentration both before and during the forest burning. The concentration of other VOCs measured before the forest burning is 72% of total concentration followed by alkenes (14%) and alkanes (11%). Meanwhile, the concentration of other VOCs measured during the forest burning is 56% of total concentration followed by alkanes (22%) and alkenes (20%) as shown in Figure 1. Other VOCs are Freon-12, acetylene, vinyl chloride, chloroform, CCl_4 etc. 95% of Vinyl chloride generated from anthropogenic sources is a monomer in polyvinyl chloride (PVC) production industries such as plastic, water pipe, and electrical equipment etc. Acetylene is used for lamplighter, metal welding, and fruit ripening etc. The average concentration of VOCs before the forest burning was higher than during burning because the photo-oxidation reaction between VOCs and the other compounds such as OH, O_3, and NO_3 etc. then VOCs were oxidized to be peroxy radicals which highly reactive to other compounds (NO_x, O_3, OH, RO_2) so they are changed or their toxicity is reduced e.g., OH+CO --> HO_2 +CO_2. For this reason, during the forest burning when there is a high concentration of other compounds, the photochemical reaction occurs at a high rate, and the concentration of VOCs is lower than before the forest burning. In addition, the concentration of VOCs during the day before the forest burning period was higher than at night since VOCs were mostly generated from traffic as shown in Figure 4. The results conform to the research of Ho. et.al, 2004.

Oxides of Nitrogen

The average concentration of oxides of nitrogen during the forest burning was higher than the concentration before the forest burning. The highest concentration before the forest burning was recorded at 4.00 pm and the lowest concentration at 3.00 am. The highest concentration during the forest burning was recorded at 8.00 am and the lowest concentration at 0.00 am. The higher concentration of oxide of nitrogen during the forest burning resulted from both traffic sources and biomass burning. Meanwhile, the source of an oxide of nitrogen before the forest burning period is traffic only. In addition, the photo radical reaction results in the reduction of NOx as shown in Figure 5.

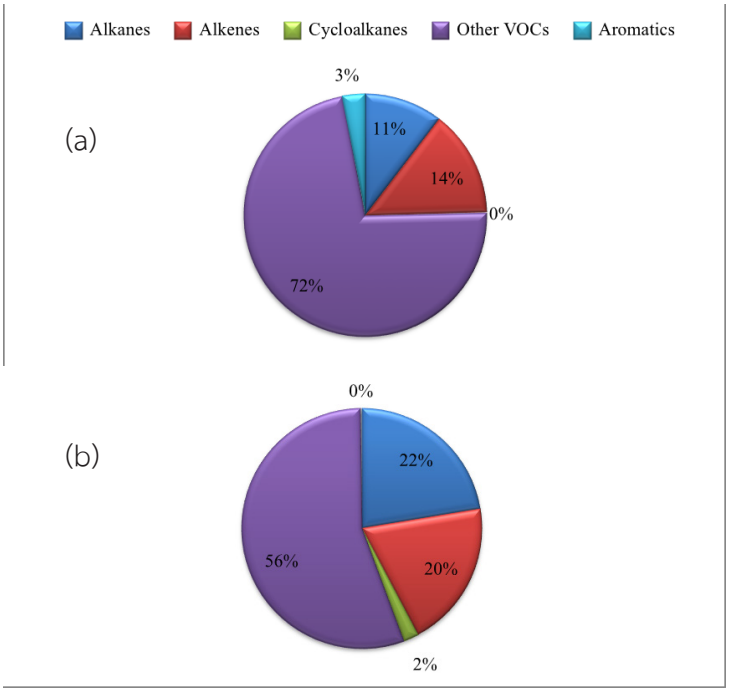


Figure 4 Proportion of five groups of VOCs; alkanes, alkenes, cycloalkanes, other VOCs and aro-matic ; (a) before the forest burning period (b) during the forest burning period

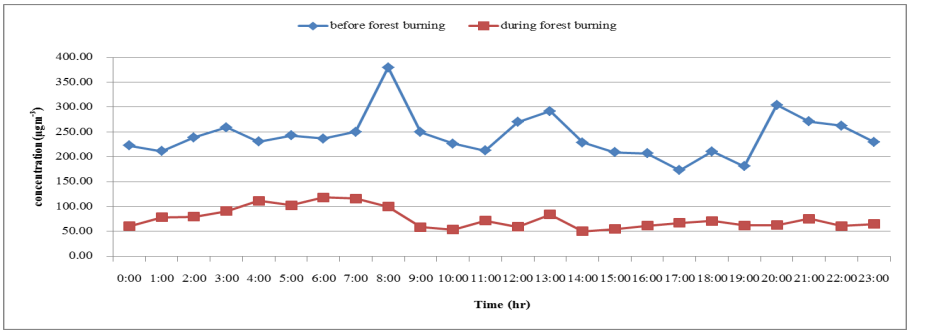


Figure 5 Concentration of VOCs in 24 hours; the blue line represents the concentration before the forest burning, the red line represents the concentration during the forest burning

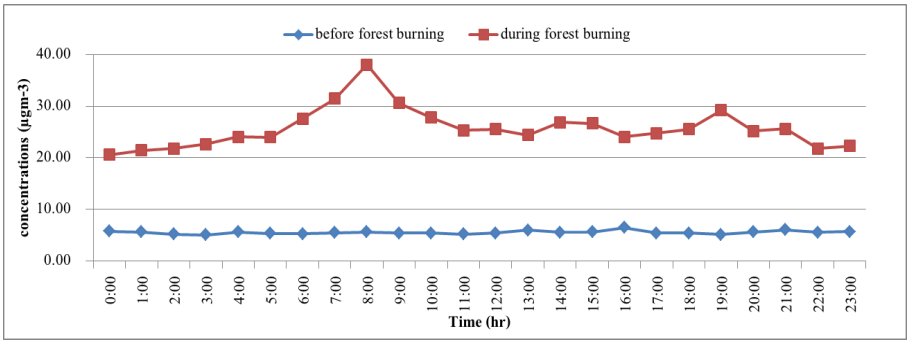


Figure 6 Concentration of oxide of nitrogen during 24 hours; the blue line represents the concentration before the forest burning, the red line represents the concentration during the forest burning

Ozone

The average concentration of ozone during the forest burning was higher than the concentration before the forest burning. The trend of ozone concentration in both periods was similar which is low during 6.00 am to 8.00 am and slightly increases until it reaches a peak in the afternoon and decreases in the evening (Alberto et al., 2013; Weihua et al., 2018) because ozone is generated from the photo radical reaction of VOCs and NOx (Surat et al., 2007). Therefore, the concentration of ozone inversely varies with the concentration of NOx as shown in Figure 6.

CONCLUSION

The results revealed that the concentration of VOCs and NO_x related to the source. Therefore, VOCs in other VOCs group (Freon-12, acetylene, vinyl chloride, chloroform, CCl_4) were detected in the highest concentration which was generated from anthropogenic sources. The average concentration of VOCs before the forest burning was higher than during burning because of the photo-oxidation reaction between VOCs and the other compounds.

The concentration of VOCs during the day before the forest burning period was higher than at night since VOCs were mostly generated from traffic

The higher concentration of oxides of nitrogen during the forest burning resulted from the accumulation of oxides of nitrogen from both traffic and biomass burning.

The average concentration of ozone in both periods was similar and is low during 6.00 am to 8.00 am and slightly increases until it reaches a peak in the afternoon and decreases in the evening.

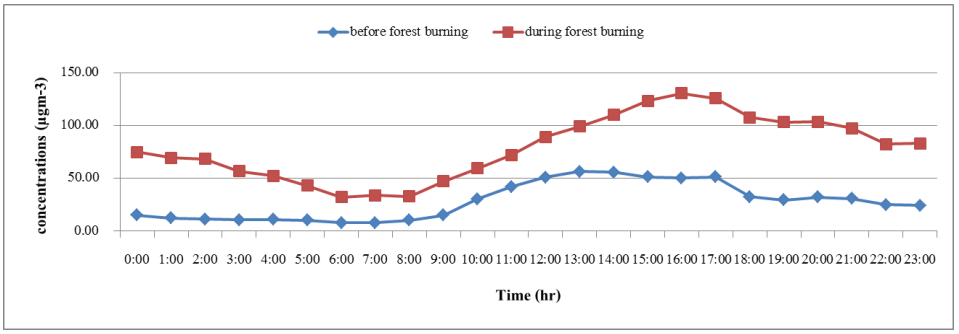


Figure 7 Concentration of ozone during 24 hours; the blue line represents the concentration before the forest burning, the red line represents the concentration during the forest burning

The tendency of ozone to rise during smog processes might be a result of an oxide of nitrogen increasing, which is ozone's precursor.

Traffic and biomass burning sources cause diseases of respiratory health effects to local residents which should be of concern to everyone and should be addressed through continuous environmental monitoring by Government and non-government agencies, together with the monitoring of human health. Timely intervention measures should be planned for safeguarding the health of the local residents and to reduce emissions of harmful biomass combustion products to protect public health.

ACKNOWLEDGMENTS

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