CHAPTER 2

Experimental

2.1 Chemicals

1) Ethylene glycol ($HOCH_2$, 62.07), Ajax Finechem, Australia
2) Nitrate standard solution (1000 ppm), Merck, Germany
3) Sodium bicarbonate ($NaHCO_3$, 84.01), 99.7%, Carlo Erba, Italy
4) Sodium carbonate (Na_2CO_3, 105.99), 99.7%, Carlo Erba, Italy
5) Sodium nitrite ($NaNO_2$, 69.00), 97%, Ajax Finechem, Australia
6) Sulfuric acid (H_2SO_4, 98.08), 95-97%, Merck, Germany
7) Deionized water

2.2 Apparatus

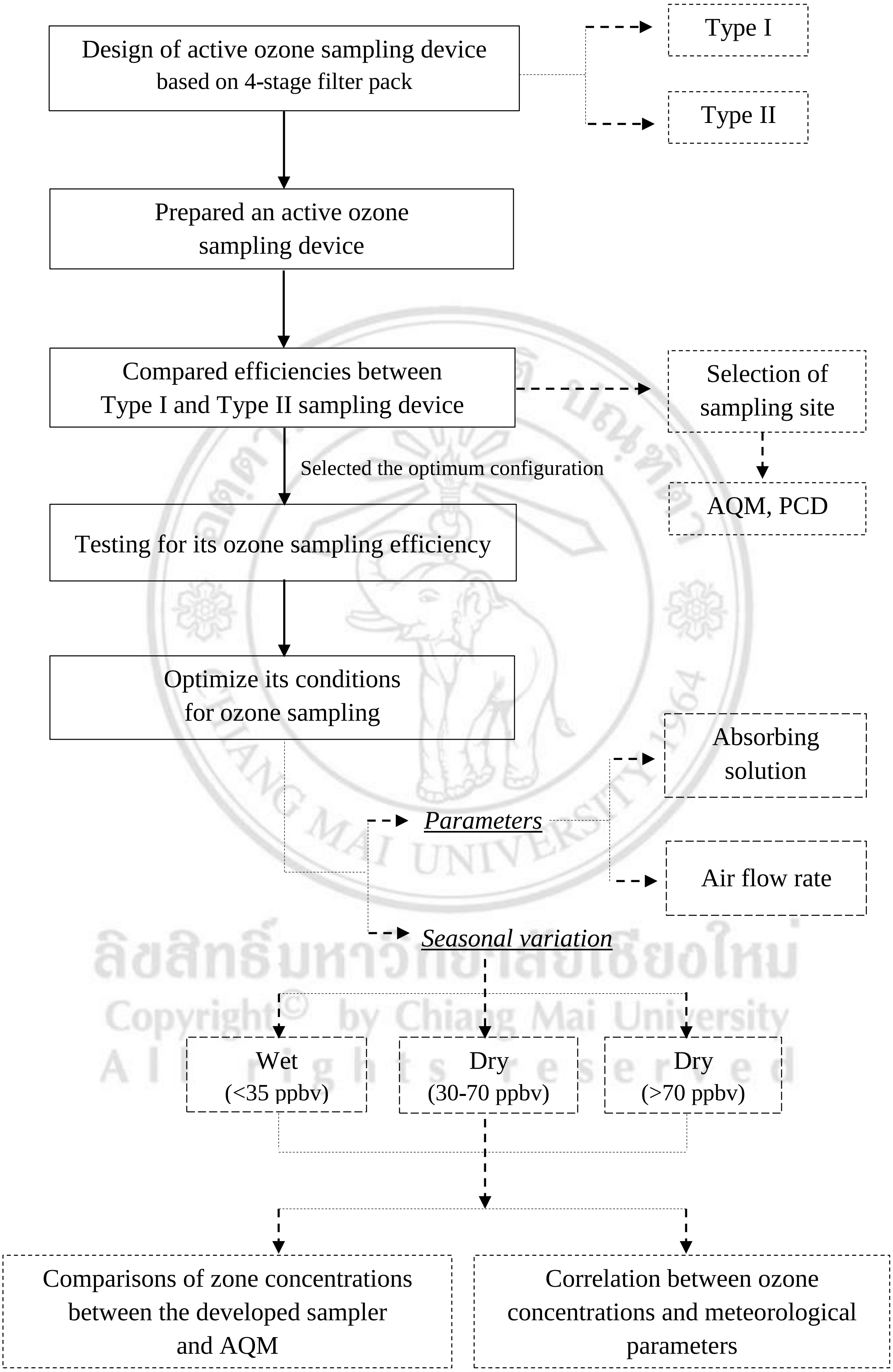
1) Four-stage filter pack, Nilu, Norway
2) GF/A filter paper, Pore size 1.6 µm, Diameter 47 mm, Whatman, USA
3) Tissue paper
4) Pump, oil-less vacuum pump DP-90V
5) Flow meter, K-100 Series Rotamete, Well,
6) Plastic tube
7) Shelter
8) 50, 100, 250 mL beaker, Duran, Germany
9) 100 mL volumetric flask, Duran, Germany
10) 2, 5, 10 mL pipette, Precicolor HBG, Germany
11) Plastic petri dish
12) Plastic tweezers
13) Aluminum-foil
14) Syringe filter, 0.45 µm cellulose acetate, chrom Tech, Inc., England
15) Parafin oil film, Para film, USA

17) 25 mL polyethylene bottles
18) Ultrasonic bath, transonic Digital S, Elma, USA
19) Ultrasonic bath, model 8891, Cole-Parmer Instrument Co., USA
20) Analytical balance, Sartorius Basic BA 210s, Germany
21) Stirring Rod
22) Spatula

2.3 Instruments

1) Ion Chromatograph (Metrohm, Switzerland)

    - Anion separation column ; Metrosep A Supp 5 column
    - Anion duard column ; Metrosep A Supp 4/5 guard
    - Interface ; 762 IC interface
    - Detector ; 732 IC detector
    - Suppresor ; self generator suppressor
    - 752 unit pump for H_2SO_4 to suppressor
    - 709 IC pump for mobile phase
    - IC net 2.3 program


Design of active ozone sampling device
based on 4-stage filter pack
Type I
Type II
Prepared an active ozone sampling device
Compared efficiencies between Type I and Type II sampling device
Selection of sampling site
AQM, PCD
Selected the optimum configuration
Testing for its ozone sampling efficiency
Optimize its conditions for ozone sampling
Absorbing solution
Parameters
Air flow rate
Seasonal variation
Wet
(<35 ppbv)
Dry
(30-70 ppbv)
Dry
(>70 ppbv)
Comparisons of zone concentrations between the developed sampler and AQM
Correlation between ozone concentrations and meteorological parameters

2.4 Development of active ozone sampling device

Ozone is highly reactive and unstable toxic gas (Helalen *et al*., 2002). Many researchers tried to improve methods for measuring ambient ozone to be simple, cost effective and efficient. The sampling method either passive or active sampling methods can be adapted and developed. However, passive sampling method depends on free flow of gases or natural gas diffusion to the sampling media. Therefore, it requires long exposure time, can easily be contaminated resulting in high interferences. Moreover, it can also be affected by meteorological conditions during the sampling. To solve those problems, an active sampler has been developed in this study by using an air pump to control a flow rate and to pull air through collecting filters. Active sampling requires low sampling period, which can improve detection limit and less dependence from meteorological conditions. This developed active sampling method was designed to collect ambient ozone on the impregnated filters. The detection limit is better than passive sampling methods but the method is more labor intensive and still needs a special equipment such as a high precision electric pump.

An active ozone sampling device (AOSD) so-called 2-stage filter pack (Figure 2.1) was adapted from a 4-stage filter pack (Nilu, Norway) (Figure 2.2) and being used for atmospheric dry deposition monitoring. The monitoring using filter-pack method has been widely conducted all over the world. Moreover, the advantage of filter pack is to simultaneously determine gases and chemical components in particulate matter (EANET, 2003).

The 2-stage filter pack was set to collect ambient ozone on the impregnated filters. It consists of 2-stage filter pack containing two collecting filters impregnated with absorbing solution (a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol) (Helalen *et al*., 2002) and connected to a pump to draw air through the collecting filters.

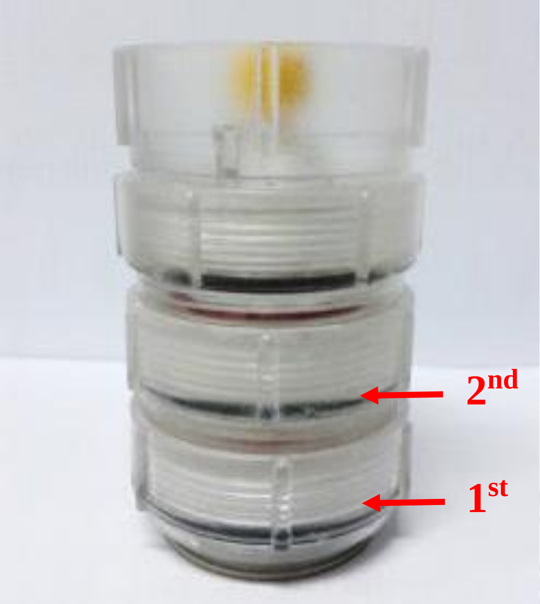


Figure 2.1 The 2-stage filter pack

Figure 2.2 NILU filter holder (4 stage, open face) (EANET, 2003)

2.4.1 Design of active ozone sampling device

The AOSD was designed for testing of the device efficiency. The sampling was conducted for 3 hours on the 2nd rooftop of Chemistry Building 2 (CB2) during 7-10 am and 2-5 pm (March - May, 2014).

2.4.1.1 Ozone sampling device; type I

The type I of AOSD (Figure 2.3) consists of 2 parts, (1) a plastic box containing 2-stage filter pack wrapped with an aluminum foil and connected to air flow meter and pump, and (2) plastic tube connecting to a plastic funnel. Air was drawn into a plastic tube (set at about 1.5 m above ground) through the collecting filters by pump. Air flow rate was controlled by a flow meter.

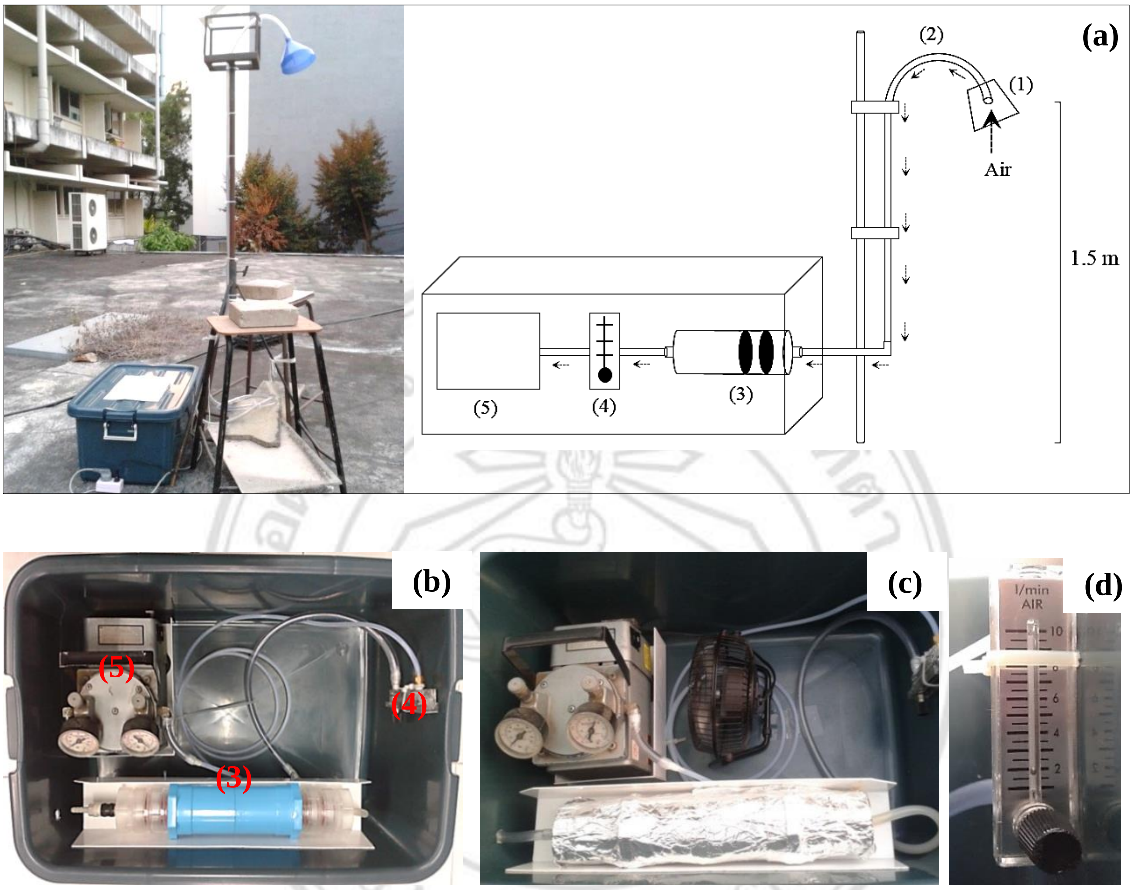


Figure 2.3 Type I of AOSD; (a) device diagram including (1) plastic funnel, (2) plastic tube, (3) 2-stage filter pack holder, (4) flow meter and (5) pump, (b) 2-stage filter pack connected to flow meter and pump packed inside a plastic box, (c) 2-stage filter pack wrapped with an aluminum foil during the sampling and (d) flow meter (1 to 10 L/min)

2.4.1.2 Ozone sampling device; type II

The type II of AOSD (Figure 2.4) was modified from type I to resolve the problem of less absorbing ozone on the collecting filters, which was probably due to too low volume of air was drawn into a sampling device. The diameter of a plastic tube was too small (10 mm) and tube was too long (1.5 m). Therefore, the 2-stage filter pack was moved and placed at the end of a plastic tube, so the air was directly in touch with the equipment (Figure 2.4a). The type II of AOSD consists of 2 parts, (1) the 2-stage filter pack covered by a plastic bucket and (2) air flow meter and pump packed inside a plastic container. The 2-stage filter pack was connected to a system and a pump to draw air through the collecting filters. This 2-stage filter pack was wrapped with an aluminum foil and placed in the shelter in order to protect it from rain and sunlight. A position of the filter pack is about 1.5 m above ground.

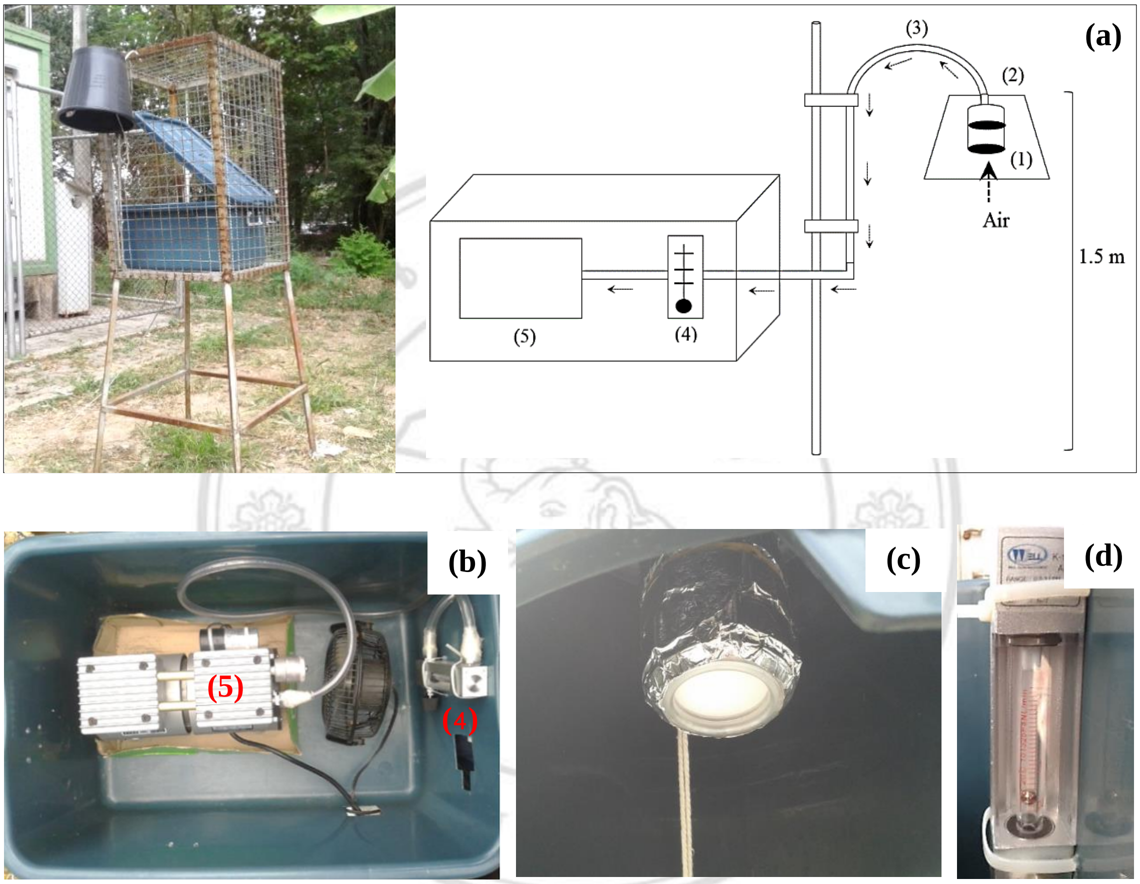


Figure 2.4 Type II of AOSD; (a) device diagram including (1) 2-stage filter pack holder, (2) shelter, (3) plastic tube, (4) flow meter and (5) pump, (b) flow meter and pump packed inside a plastic box, (c) 2-stage filter pack wrapped with an aluminum foil packed inside the shelter and (d) flow meter (range: 0.3 to 3.0 L/min)

After that, the optimum of configuration of AOSD was selected to test optimum conditions for ozone sampling under difference ozone concentrations in the ambient air.

2.5 Ozone sampling and analysis

2.5.1 Preparation of AOSD

2.5.1.1 Sampler (NILU, Norway)

All the filter pack components were cleaned up by 30 mins. sonicating and rinsed twice with deionized (DI) water before drying at 40 °C overnight. The filter pack can be reused after cleaning following the above instruction.

2.5.1.2 Sorbent

The sorbent used in this experiment was the glass filter paper (Whatman GF/A; pore size: 1.6 µm diameter: 47 mm) which is a circle with a same size of an inner diameter of the filter pack (47 mm).

2.5.2 Preparation of collection filters

Ambient ozone was collected by using filters coated with a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol. NO_2^- was used as ozone sorbent through a mechanism that NO_2^- was oxidized by ozone to form NO_3^- on the collecting filter ($NO_2^- + O_3 \rightarrow NO_3^- + O_2$). Na_2CO_3 was used to maintain pH values of the collecting medium to be alkaline because the reaction between NO_2^- and ozone is pH dependent with a rate constant that increases with pH (Helalen *et al.*, 2002). Ethylene glycol was used as a hygroscopic compound to keep the absorbing solution at constant humidity because water molecules enhance the oxidation reaction of NO_2^- by ozone (Koutrakis *et al.*, 1993; Helalen *et al.*, 2002).

The steps of collection filter preparation according to use of 4-stage filter pack (EANET, 2003) are shown in Figure 2.5. The absorbing solution was prepared by using a mix of $NaNO_2$, Na_2CO_3, and ethylene glycol (1:1:10) at various concentrations (Table 2.1) in 100 ml DI water. After that, the solution was poured into 3 beakers (NO.1-3). The fiber filter was hold by a plastic tweezer and soaked in the absorbing solution in those 3 beakers one by one, in order to clean the filter and to be coated. It was then put between two sheets of a large cellulose sheet to absorb extra water from the impregnated filter and kept in a pettri dish. The impregnated filters were mounted in the 2-stage filter pack. Then, it was wrapped with an aluminum foil. Prior to exposure, the 2-stage filter pack was sealed in a plastic zip lock bag and placed in a plastic container.

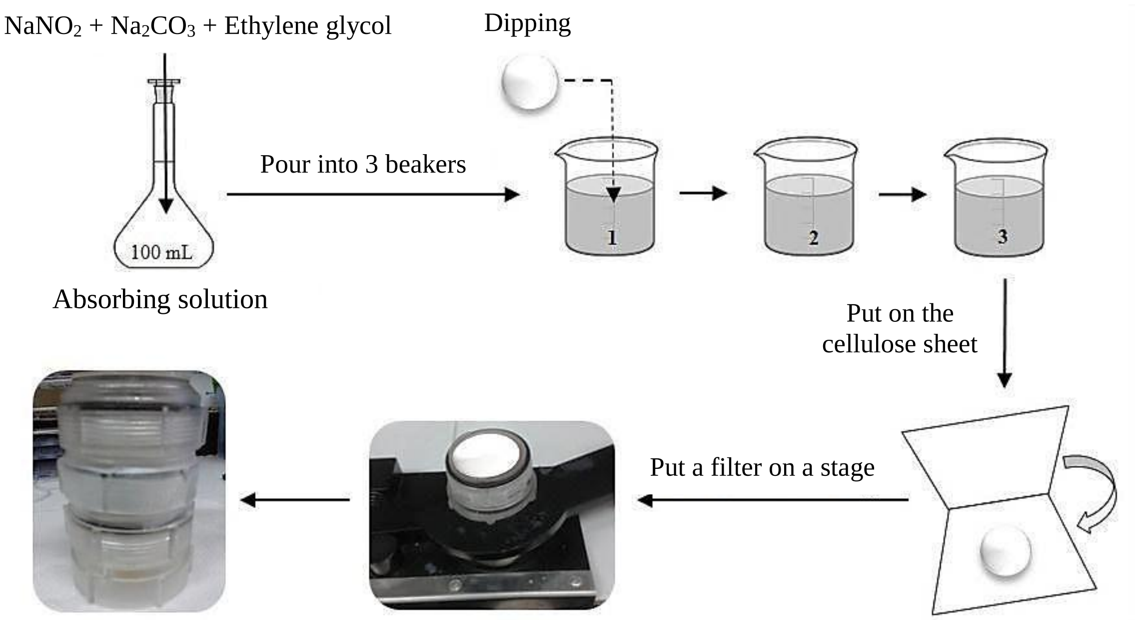


Figure 2.5 Preparation diagram of collection filters

2.5.3 Ozone sampling

A pump was opened about 10 mins. prior to exposure. Then, air flow rate was set at various air flows (Table 2.1). The sampling was started by removal of the sampler cap out and then connected the sampler to the plastic tube, which connected to a pump. The sampling was conducted for 1 hour in the morning and in the afternoon at the site nearby the air quality monitoring station (AQM) of the Pollution Control Department (PCD).

2.5.4 Ozone analysis

After the sampling, the filters were extracted with 10 mL DI water using the ultrasonicator for 30 mins. at room temperature (25-29 °C). After extraction process, the solution was filtered through 0.45 μm cellulose filter with helping of syringe in order to get rid of contaminated particles, which could disturb measurement and analyzed for NO_3^- by ion chromatograph (IC) (Metrohm, Switzerland) with A supp 5 column. The eluent was a mix of 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$ buffer and 100 mM H_2SO_4 suppressor.

2.5.5 Calculation of ozone concentrations

Ozone concentration; C_{O_3} (ppbv) collected by the active sampling device, can be calculated according to Geyh *et al*., 1999.

$$C_{O_3} = \frac{C_{NO_3^-} \times V \times CF \times K}{CR \times T \times MW_{NO_3^-}} \qquad (1)$$

where $C_{NO_3^-}$ is the nitrate concentrations (sample - blank, µg/mL), V is the extraction volume (mL), CF is the conversion factor 10^6 (cm^3/m^3), K is conversion constant (24.46 ppbv/(µg/m^3)) at 1 atm and 25 °C, CR is collection rate (cm^3/min) equals to the measured pump flow rate (L/min) x 10^3 (cm^3/L), T is the exposure time (mins), $MW_{NO_3^-}$ is the molecular weight of the nitrate ion (62 µg/µmol).

2.6 Design for ozone sampling period under different ozone concentrations

2.6.1 Selection of sampling period

According to 3 years (2012-2014) tropospheric ozone data of the PCD air quality monitoring (AQM) station in Chiang Mai City, ozone concentrations were high in dry season and low in wet season (Figure 2.6). Ozone concentrations were divided into low (<35 ppbv), moderate (30-70 ppbv) and high (>70 ppbv) as shown in Figure 2.7. Low levels was found in wet season (June - October), while moderate and high levels were found in cool dry period (November - February) and hot dry period (March - May), respectively. Figure 2.7 show the pattern of ozone concentrations throughout the day. It showed that ozone concentrations begin to rise in the morning (~10-12 am) and then decrease after noon (~1-6 pm). Therefore, the sampling was conducted in the morning (10-12 am) and in the afternoon (2-4 pm) based on ozone level as well as seasonal variation.

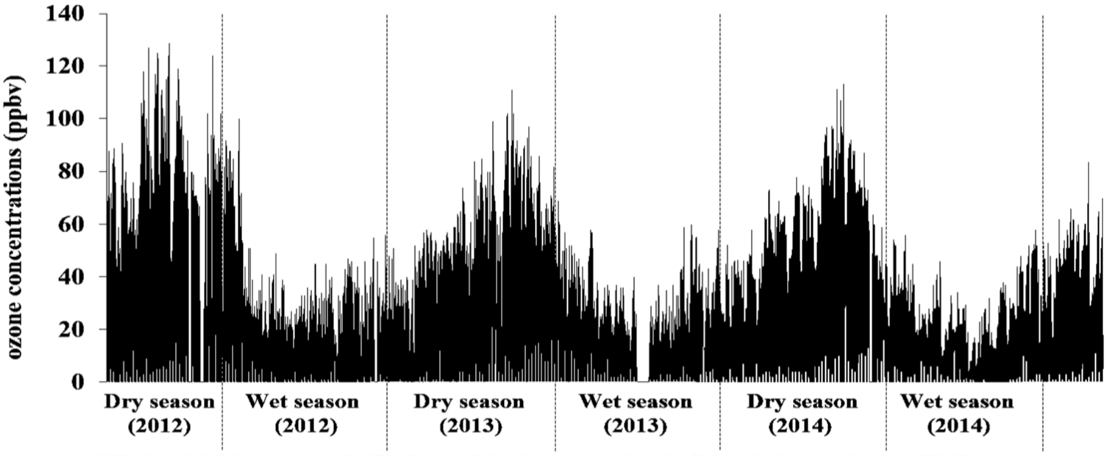


Figure 2.6 Three years (2012-2014) hourly ozone concentrations in each season in Chiang Mai Province

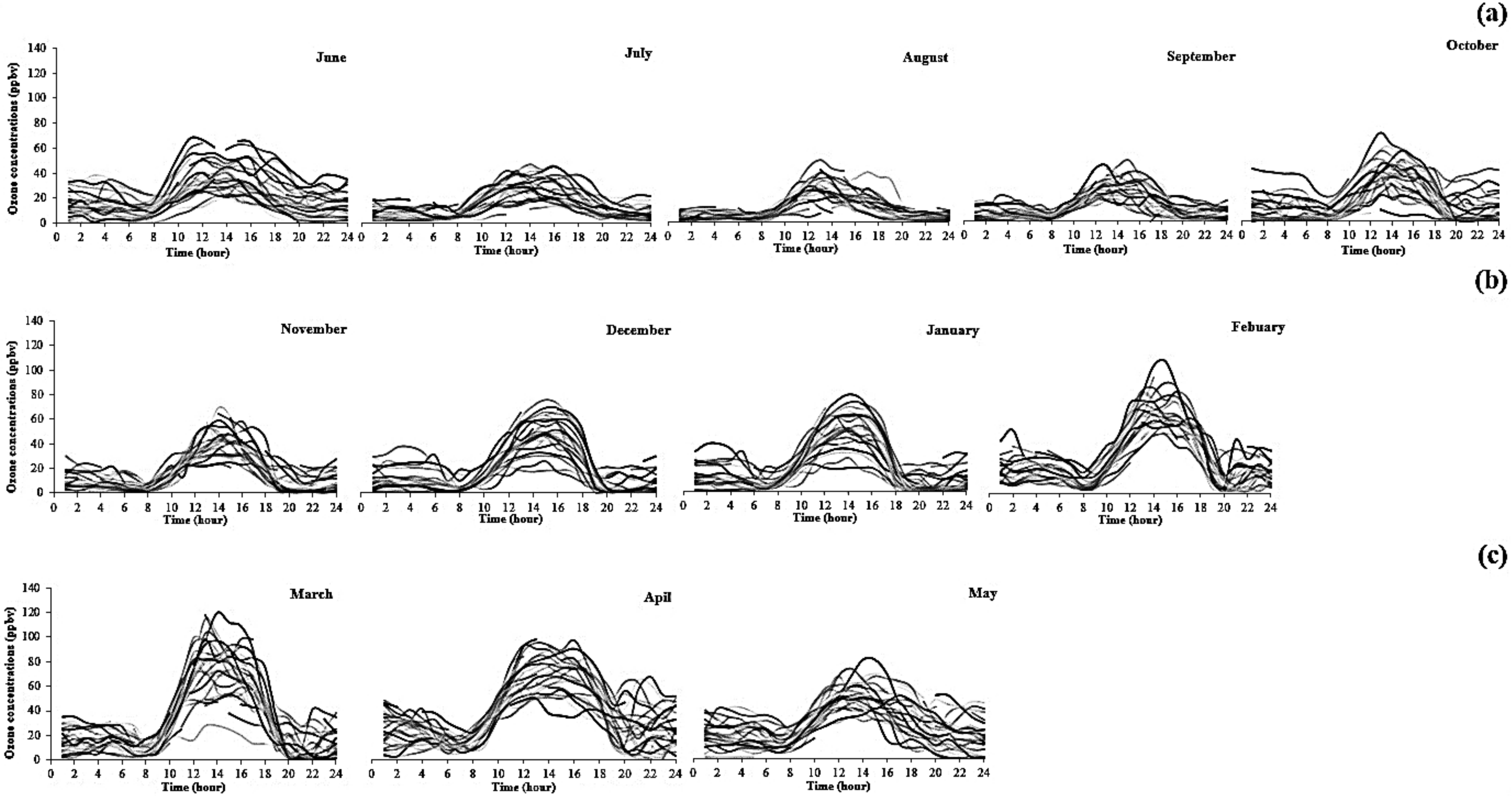


Figure 2.7 Ozone concentrations within 24 hours in each month (2013); (a) Low ozone concentration in wet season (<35 ppbv) during June - October, (b) Moderate ozone concentration in dry season (30-70 ppbv) during November - February and (c) High ozone concentration in dry season (>70 ppbv) during March - May

2.6.2 Conditions for ozone sampling in the ambient air

This process was simultaneously tested with the selected sampling period. The AOSD was tested under different ozone concentrations in wet season with low ozone concentrations (<35 ppbv) and in dry season with medium ozone concentrations (30-70 ppbv) and high ozone concentrations (>70 ppbv). Optimization of affecting parameters such as air flow rate and concentrations of absorbing solution were optimized (Table 2.1)

Table 2.1 Conditions for ozone sampling in wet and dry season

Season	**Ozone concentrations**	**Conditions**	**Absorbing solution**			**Air flow rate (L/min)**
			$NaNO_2$ (% w/v)	**Na_2CO_3 (% w/v)**	**Ethylene glycol (% v/v)**	
Wet	Low (<35 ppbv)	1a (n = 8)	1.00	1.00	10.0	0.5
		2a (n = 8)	1.00	1.00	10.0	1.0
		3a (n = 8)	0.50	0.50	5.0	1.0
		4a (n = 16)	0.50	0.50	5.0	1.2
		5a (n = 16)	0.50	0.50	5.0	1.5
Dry	Medium (30-70 ppbv)	2b (n = 4)	1.00	1.00	10.0	1.2
		3b (n = 4)	0.50	0.50	5.0	1.2
		4b (n = 24)	0.50	0.50	5.0	0.5
		5b (n = 4)	0.75	0.75	7.5	0.5
		1c (n = 4)	1.00	1.00	10.0	0.5
	High (>70 ppbv)	3c (n = 24)	0.75	0.75	7.5	0.5
		4c (n = 8)	1.00	1.00	10.0	0.5
		1a (n = 8)	1.25	1.25	12.5	0.5
		2a (n = 8)	1.50	1.50	15.0	0.5

2.7 Ozone sampling sites

The Ozone sampling method was compared with the standard method measured by chemiluminescent technique for testing the optimum conditions for ozone sampling in ambient air. The sampling sites were selected based on the position of the air quality monitoring station (AQM) of PCD in Chiang Mai City (Figure 2.8). The first sampling site was at Yupparaj Wittayalai School (YP site), which was an open area and surrounded by buildings (Figure 2.9). This site is located inside the Chiang Mai City, surrounded by community including school, temples, government offices and business building etc. Due to some technical problem, the AQM at YP station was stopped the ozone measurement since 21st August 2014. Therefore, the sampling site was moved to the Chiang Mai City hall (CH site) in dry season, which is parking area and surrounded by big trees (Figure 2.10). This site is located in the North-West the city.

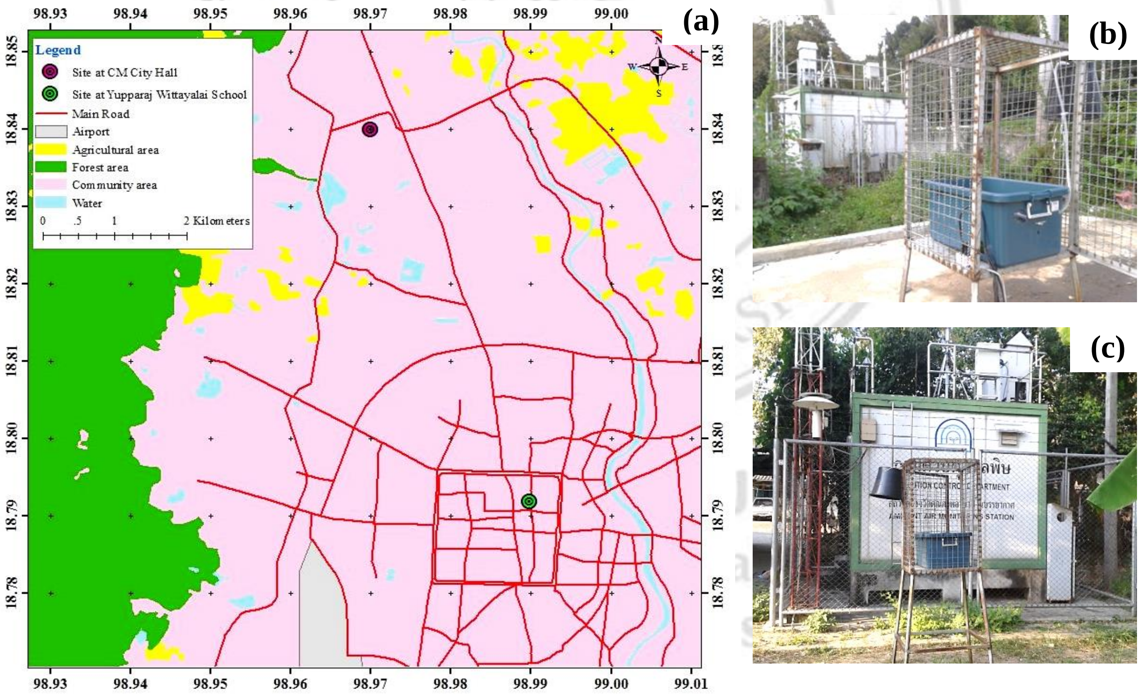


Figure 2.8 Information of sampling areas (a) Land use map around sampling areas, (b) YP site and (c) CH site

Figure 2.9 Surrounding area of YP site

Figure 2.10 Surrounding area of CH site

2.8 Validation of active ozone sampling device

2.8.1 Percent differences (%D)

Considering of the similarity of the ozone measurements from two different methods by expressed as %D, which is calculated by equation (2).

$$\%D = \frac{(x_1 - x_2)}{(x_1 + x_2)/2} \times 100 \qquad (2)$$

Where x_1 is the ozone concentration (ppbv) obtained from the developed AOSD and x_2 is the ozone concentration (ppbv) obtained from the AQM.

2.8.2 Efficiency of the developed AOSD

The efficiency of the developed AOSD was considered by comparison between an hourly ozone concentrations from the developed AOSD with the measured values reported from the AQM.

The efficiency is expressed as the ozone ratio, which is calculated by equation (3).

$$ratio = \frac{x_1}{x_2} \qquad (3)$$

Where x_1 is the ozone concentration (ppbv) obtained from the developed AOSD and x_2 is the ozone concentration (ppbv) obtained from the AQM.

2.9 Statistical analysis

Pair t-test was used for comparison of ozone concentrations between the developed sampling method and the AQM both in wet and dry seasons. Pearson correlation (r) was used to identify relationships between ozone concentrations and meteorological parameters.

2.10 Limit of detection (LOD) of active sampling method

The limit of detection of method; LOD_{method} (ppbv · h) collected by the AOSD, can be calculated according to Geyh *et al*., 1997.

$$LOD_{method} = \frac{3\sigma_{NO_3^-} \times V \times CF \times K}{CR \times MW_{NO_3^-}} \quad (4)$$

where LOD_{method} is detection limit of method (ppb·h), $\sigma_{NO_3^-}$ is the standard deviation of nitrate concentration from test blanks (µg/mL), V is the extraction volume (mL), CF is the conversion factor 10^6 (cm^3/m^3), K is conversion constant (24.46 ppbv/(µg/m^3)) at 1 atm and 298 K, CR is collection rate (cm^3/min) equals to the measured pump flow rate (L/min) x 10^3 (cm^3/L), $MW_{NO_3^-}$ is the molecular weight of the nitrate ion (62 µg/µmol)