CHAPTER 3

Results and discussion

The active ozone sampling device (AOSD) was developed. Two types of device configurations were tested and compared under different conditions; wet season with low ozone concentrations (<35 ppbv) and dry season with medium ozone concentrations (30-70 ppbv) and higher ozone concentrations (>70 ppbv). The developed active ozone sampling method was compared with the standard method measured by chemiluminescence technique at the AQM station.

3.1 The optimum configuration of active ozone sampling device

The efficiency of the device was tested by comparing positions of the 2-stage filter pack. The type I, the one end of the 2-stage filter pack was connected to a plastic tube and the other end was connected to the flow meter and a pump as already described in Chapter 2. Air was drawn into a plastic tube through the collecting filters by a pump (Figure 2.3). For type II, the position of the 2-stage filter pack was set outside the plastic container and exposed directly to ambient air (Figure 2.4).

Both configuration types were tested by varying concentrations of the absorbing solution and air flow rates. The sampling period was 3 hours. Ozone concentrations in each condition and in each sampler type were compared with the reference values of AQM (Figure 3.1). The measured ozone concentrations are presented as 1^{st} and 2^{nd} stages according to the sampling device.

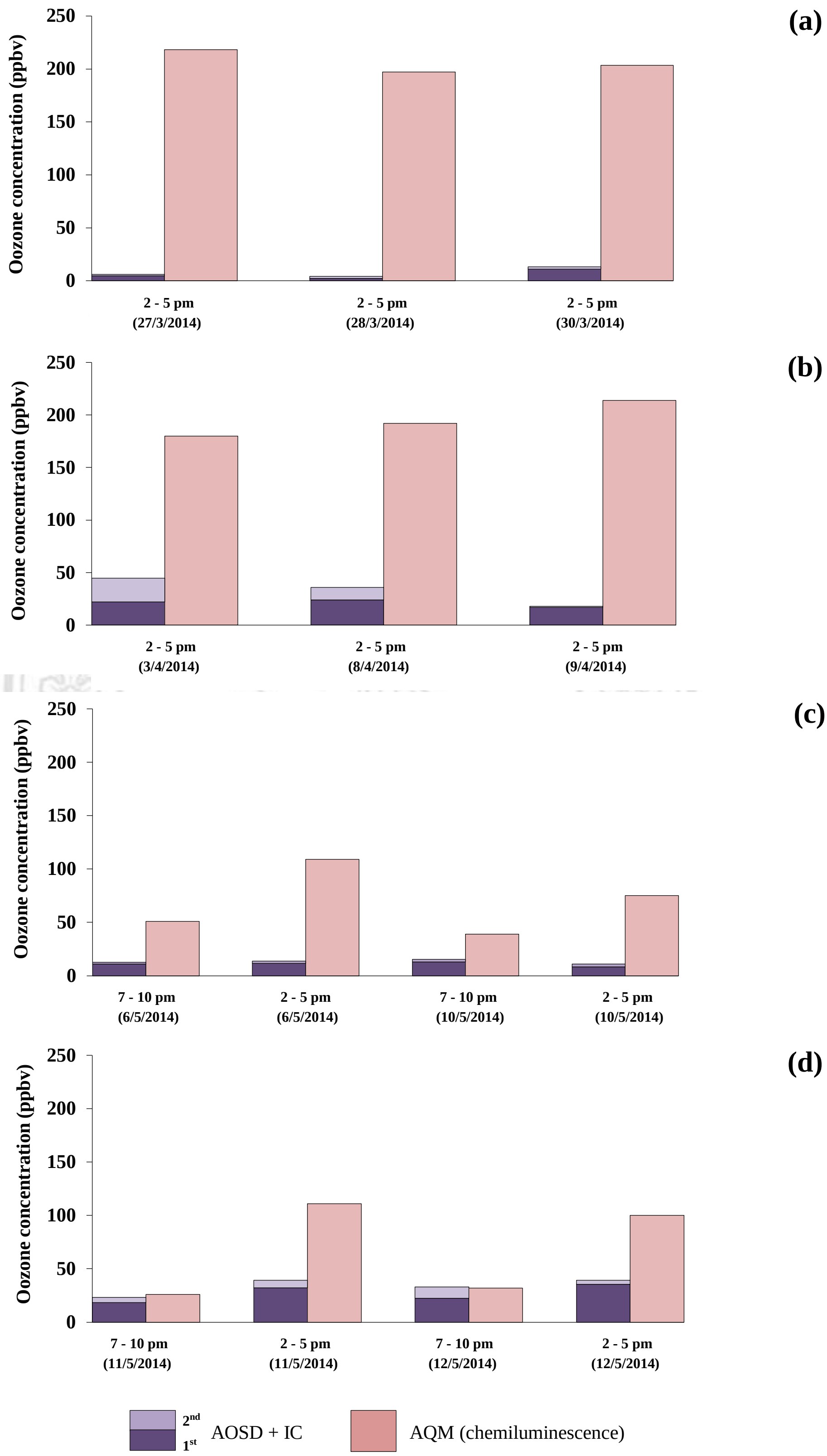


Figure 3.1 Ozone concentrations (3-hr) obtained from the same absorbing solution (0.1 % $NaNO_2$/ 0.1 % Na_2CO_3/ 1% ethylene glycol) with different air flow rates (L/min) (a) 2.0, (b) 1.5, (c) 1.0 and (d) 0.5

The results showed that the type II (Figure 3.1c - d) of AOSD was better than the type I (Figure 3.1a - b). The configuration of AOSD in the type I depends on the amount of air drawn into a plastic tube through the collecting filters by pump. However, the diameter of a plastic tube is quite small (10 mm) but long (1.5 m). Therefore, the amount of air drawn into a plastic tube through the collecting filters was lower than, when the filter was exposed directly as the type II. In addition, the scale of air flow rate used in the type I ranged from 1 to 10 L/min, which its resolution was low. So, it may be not suitable.

Table 3.1 Performance of the AOSD comparing with AQM based on ozone concentrations

Types of AOSD	Conditions	Ozone concentrations (ppbv)		(1)/(2)
		Developed sampling device (1)	Reference values from AQM (2)	
I	a (n = 3)	8 ± 5	206 ± 11	0.04
	b (n = 3)	33 ± 14	195 ± 17	0.17
II	c (n = 4)	13 ± 2	69 ± 31	0.19
	d (n = 4)	34 ± 8	67 ± 44	**0.50**

a = 0.1 % $NaNO_2$/ 0.1 % Na_2CO_3/ 1% ethylene glycol + 2.0 L/min

b = 0.1 % $NaNO_2$/ 0.1 % Na_2CO_3/ 1% ethylene glycol + 1.5 L/min

c = 0.1 % $NaNO_2$/ 0.1 % Na_2CO_3/ 1% ethylene glycol + 1.0 L/min

d = 0.1 % $NaNO_2$/ 0.1 % Na_2CO_3/ 1% ethylene glycol + 0.5 L/min

Table 3.1 shows performance of the AOSD comparing with AQM based on ozone concentrations. It was found that the condition No. 4 of the AOSD type II showed a better result comparing with the reference values (ratios = 0.50). Therefore, it can be concluded that the type II was more effective for ozone sampling than type I.

3.2 Performance of the developed active ozone sampling device

After selection of the effective AOSD (type II), the condition (0.1% $NaNO_2$/ 0.1% Na_2CO_3/ 1% ethylene glycol as absorbing solution and 0.5 L/min of air flow rate) was tested again at the AQM station, Yupparaj Wittayalai School, Chiang Mai. The sampling was carried out for 3 hours on May, 2014. The 3 hours ozone concentrations from the developed AOSD were compared with reference values from the AQM station as shown in Figure 3.2. The ratios of average ozone concentrations obtained from the developed AOSD and the reference values are shown in Table 3.2.

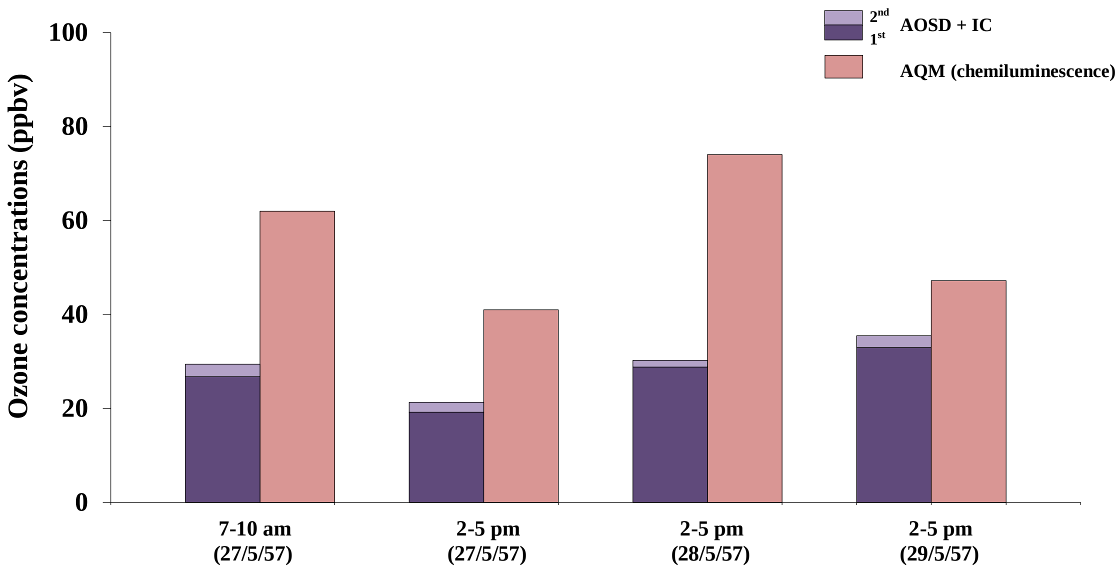


Figure 3.2 Comparison of 3-hr ozone concentrations of developed AOSD with reference values from the AQM

Table 3.2 Comparison of the average ozone concentrations obtained from the developed AOSD and the reference values

Ozone concentrations (ppbv)		
Developed sampling device (n = 4) (1)	**Reference values from AQM (n = 4) (2)**	**(1)/(2)**
29 ± 5	56 ± 13	**0.52**

It was found that the developed AOSD was less effective than the AQM when comparing the ozone concentrations (~50%). This is probably due to capacity of the developed device. Therefore, the sampling period was changed from 3 hours to 1 hour. This 1 hour value is compatible with the standard value of ozone in ambient air and related with the acute human health effect. The short term ambient ozone standard of Thailand should not exceed 100 ppbv (1-hr). Therefore, the ozone sampling was conducted for every 1 hour in the morning (10-12 am) and in the afternoon (2-4 pm). However, some important parameters including adsorbing solution concentration and air flow rate were also adjusted according to ambient ozone level in wet and dry seasons.

3.3 The optimum conditions of active ozone sampling device

The AOSD was tested by varying concentrations of the ratios of absorbing solution and air flow rates (see Table 2.1, page 27) to find out for the optimum conditions for ozone sampling. The sampling was conducted for 1 hour during 10-12 am and 2-4 pm at Yupparaj Wittayalai School for wet season (June - July, 2014) and Chiang Mai City hall for dry season (November - December, 2014 and March - April, 2015) (see Appendix B). The average hourly ozone concentrations in each condition obtained from the developed active ozone sampling method were compared with the average hourly ozone concentrations (reference values) measured by chemiluminescence technique at the AQM station as shown in Figure 3.3. The ratios of ozone concentrations obtained from the developed AOSD and the reference values are shown in Table 3.3.

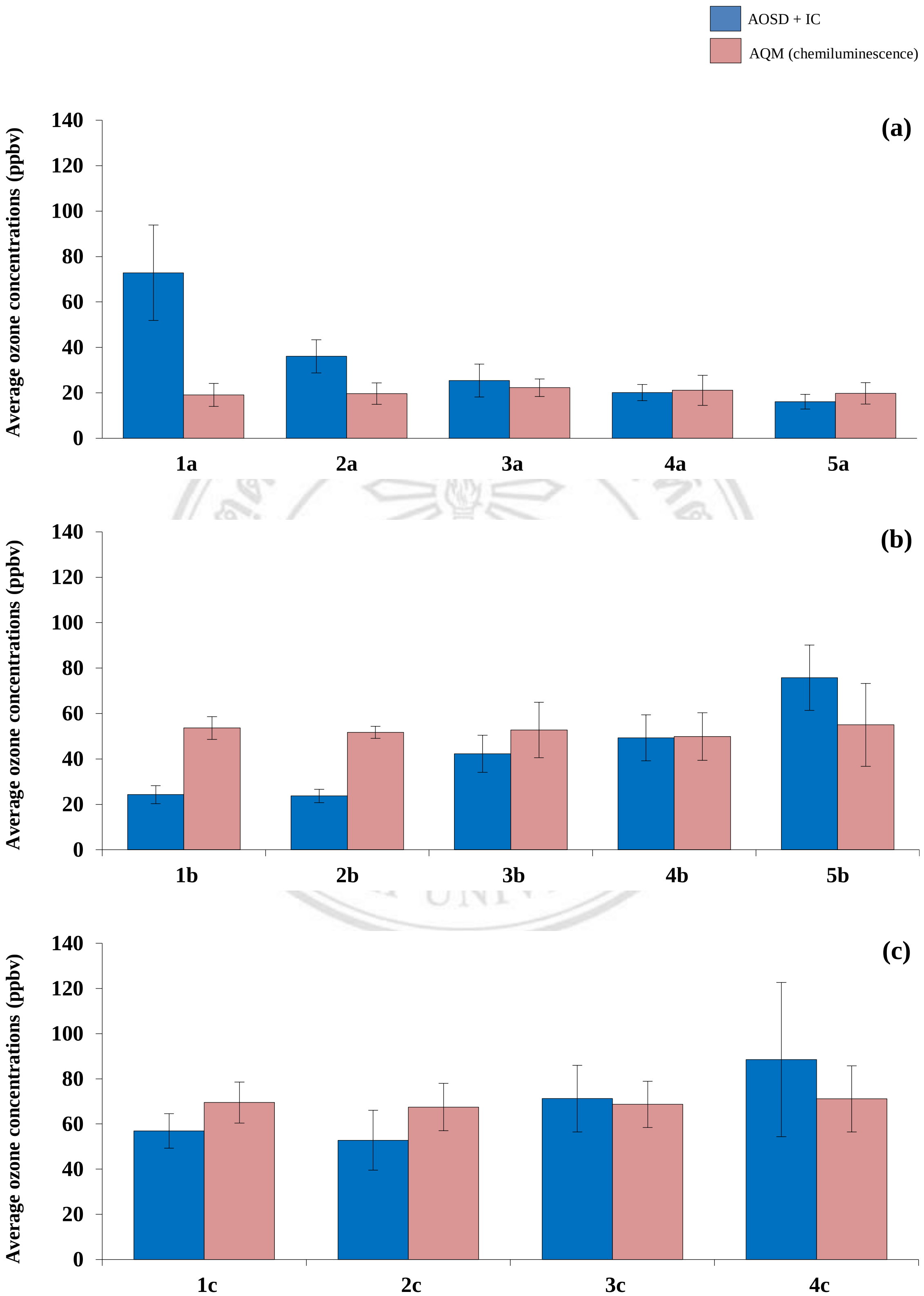


Figure 3.3 Average hourly ozone concentrations obtained from the developed AOSD at different sampling conditions and the reference values in (a) wet season (<35 ppbv), (b) dry season (30-70 ppbv) and (c) dry season (>70 ppbv)

Table 3.3 shows comparison of the average hourly ozone concentrations obtained from the developed AOSD and the reference values. It was found that during the sampling in wet season (low ozone concentration), the condition of absorbing solution used was low, while the flow rate was quite high (1.2 L/min). On the other hand when the ozone concentrations increased in dry season, the condition of absorbing solution was also high while the flow rate was low (0.5 L/min).

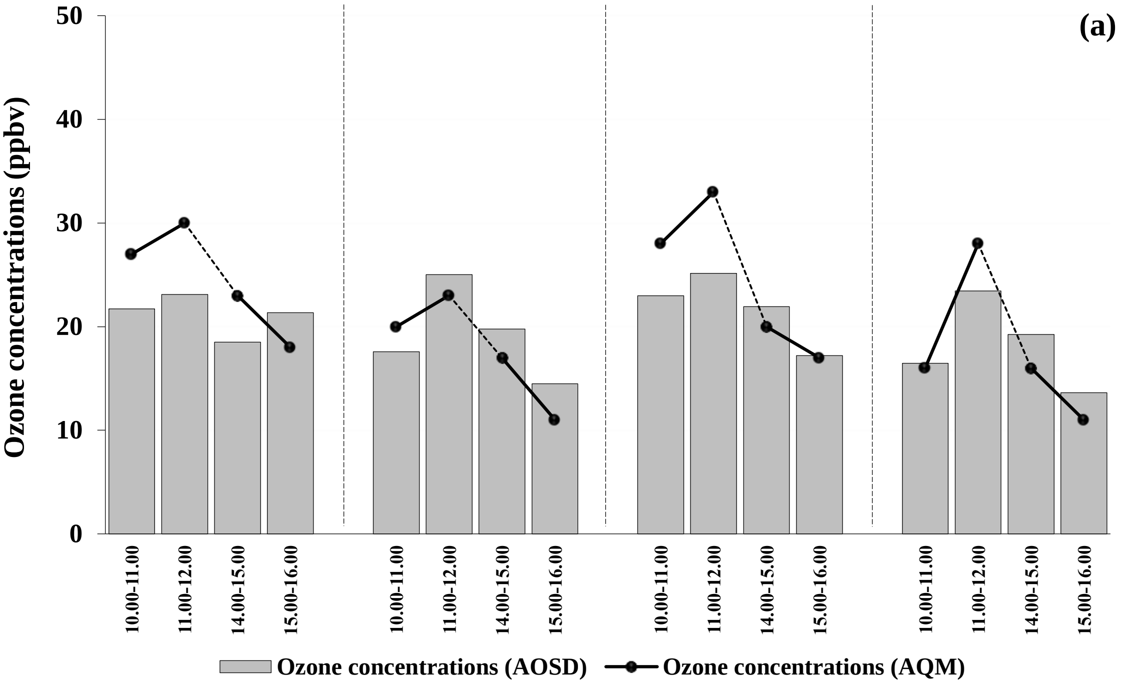
Table 3.3 Comparison of the average hourly ozone concentrations obtained from the developed AOSD and the reference values

Season	**Ozone concentrations (ppbv)**	**Conditions**	**Ozone concentrations (ppbv)**		**(1)/(2)**
			Developed sampling device (1)	**Reference values (2)**	
Wet	Low (<35 ppbv)	1a (n = 8)	73 ± 21	19 ± 5	3.82
		2a (n = 8)	36 ± 7	20 ± 5	1.84
		3a (n = 8)	25 ± 7	22 ± 4	1.14
		4a (n = 16)	20 ± 3	21 ± 6	**0.95**
		5a (n = 16)	16 ± 3	18 ± 5	0.90
Dry	Medium (30-70 ppbv)	1b (n = 8)	24 ± 4	54 ± 5	0.45
		2b (n = 4)	24 ± 3	52 ± 3	0.46
		3b (n = 4)	42 ± 8	53 ± 12	0.80
		4b (n = 24)	49 ± 10	50 ± 10	**0.99**
		5b (n = 4)	76 ± 14	55 ± 18	1.38
	High (>70 ppbv)	1c (n = 4)	57 ± 8	70 ± 9	0.82
		2c (n = 4)	53 ± 13	68 ± 10	0.78
		3c (n = 24)	71 ± 15	70 ± 10	**1.02**
		4c (n = 8)	89 ± 34	71 ± 15	1.24

Therefore, the optimum absorbing solution ratio and air flow rate for ozone sampling in wet season with low ozone concentrations (<35 ppbv) were 0.5% $NaNO_2$/ 0.5% Na_2CO_3/ 5% ethylene glycol and 1.2 L/min, while those in dry season with medium ozone concentrations (30-70 ppbv) and higher ozone concentrations (>70 ppbv) were 0.75% $NaNO_2$/ 0.75% Na_2CO_3/ 7.5% ethylene glycol and 0.5 L/min and 1.25% $NaNO_2$/ 1.25% Na_2CO_3/ 12.5% ethylene glycol and 0.5 L/min, respectively. It can be seen that concentrations of absorbing solution have to be appropriated with ozone concentrations in ambient air. In contrast, air flow rate was adjusted conversely with the ambient ozone concentrations.

The ratios of ozone concentrations obtained from the developed AOSD and the reference values under the optimum condition (highlighted in Table 3.3) were very closed to 1.00. It showed that the efficiency of the developed AOSD was very closed to the standard method (~100%). So, it revealed that the developed AOSD was efficient enough for ozone measurement under varying ozone concentrations.

Moreover, the hourly ozone values obtained from the developed AOSD following with IC analysis and from the reference technique at the AQM station under the optimum condition were not significantly different ($p > 0.05$) and well correlated both in wet season with low ozone concentrations ($r = 0.848$, $p < 0.01$) and dry season with medium ozone concentrations ($r = 0.636$, $p < 0.01$), high ozone concentrations ($r = 0.530$, $p < 0.05$).



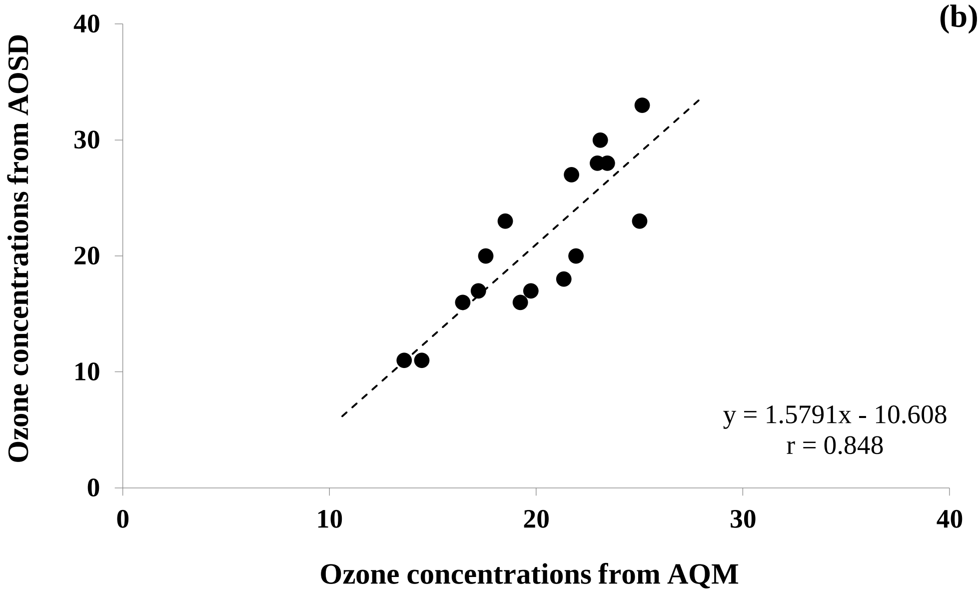


Figure 3.4 Hourly ozone concentrations in wet season (<35 ppbv) (a) Comparison of ozone obtained from AOSD and AQM (b) Correlation of ozone concentrations between AOSD and AQM

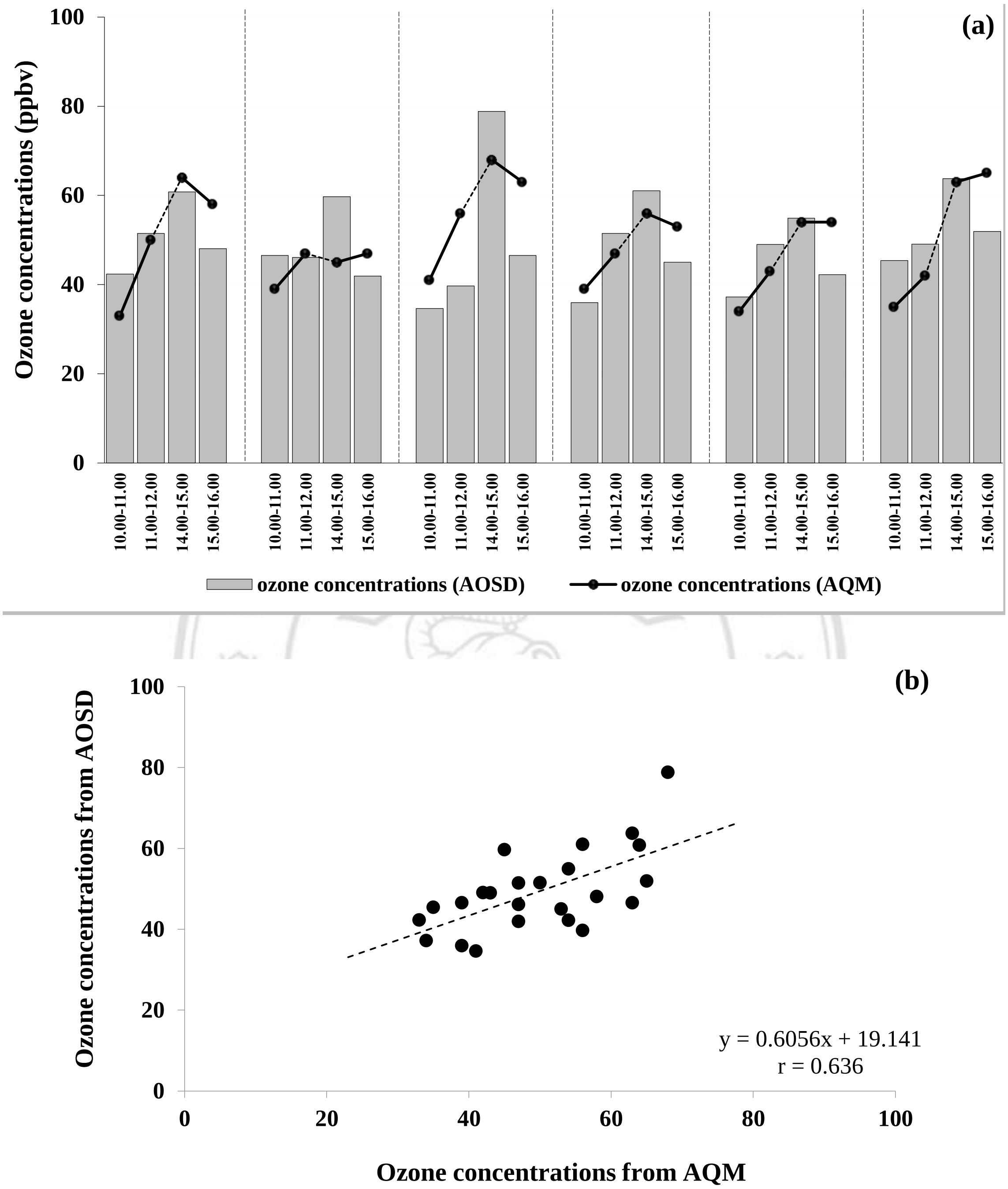


Figure 3.5 Hourly ozone concentrations in dry season (30-70 ppbv) (a) Comparison of ozone obtained from AOSD and AQM (b) Correlation of ozone concentrations between AOSD and AQM

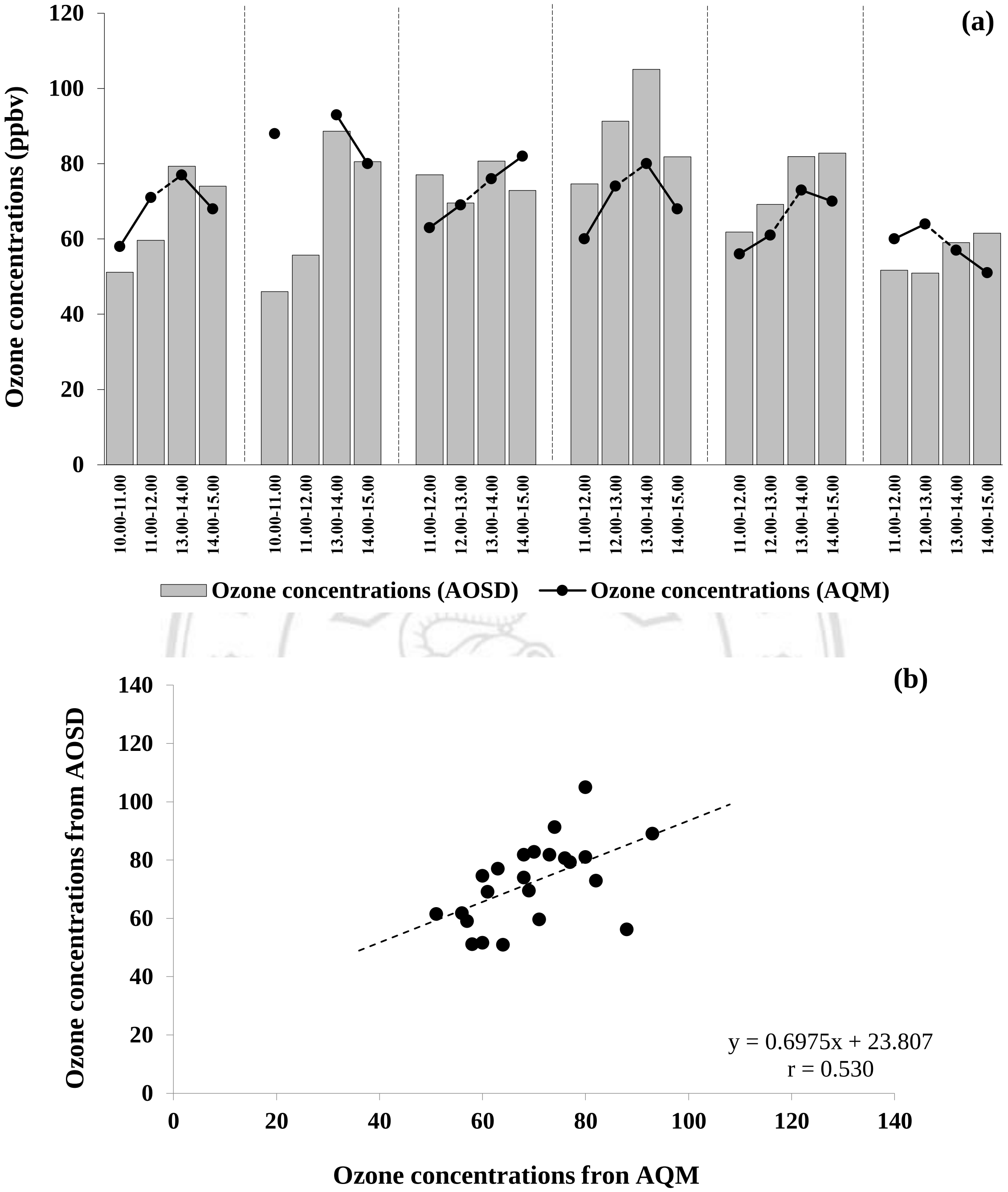


Figure 3.6 Hourly ozone concentrations in dry season (>70 ppbv) (a) Comparison of ozone obtained from AOSD and AQM (b) Correlation of ozone concentrations between AOSD and AQM

Figure 3.7 shows comparison of 1-hr ozone concentrations obtained from the developed AOSD with reference values from the AQM under the optimum conditions (see Table 3.3). The measured ozone concentrations are separated presented as the 1st and 2nd filters according to the sampling device. Total ozone concentrations in each optimum condition from AOSD were comparable to the values from the AQM. It showed that using only 1st stage filter may not be enough for ozone sampling. Therefore, the sampling needs 2-stage sampler to get measured values closed to the reference values.

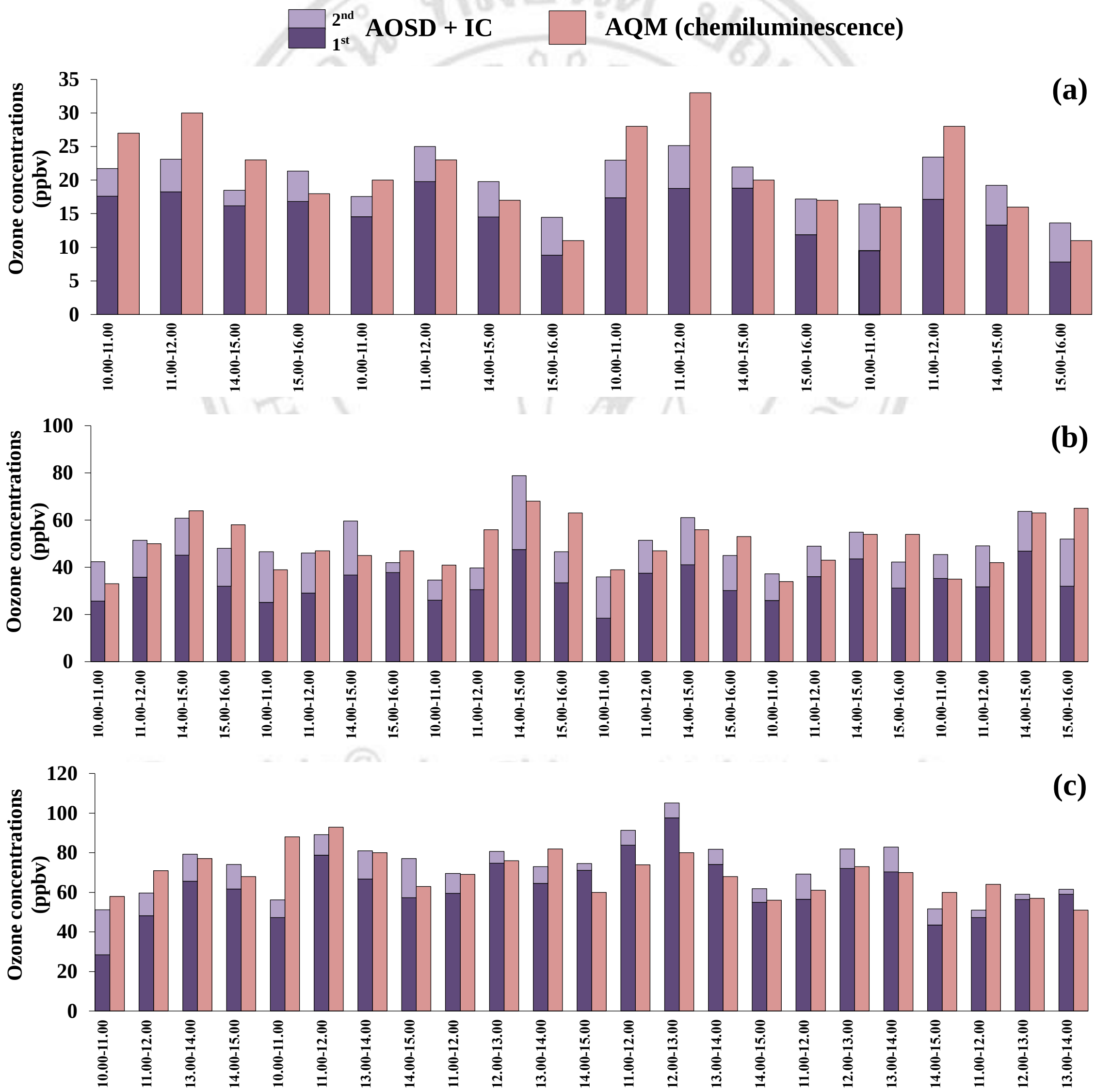


Figure 3.7 Comparison of 1-hr ozone concentrations obtained from the developed AOSD with reference values from the AQM under the optimum condition (a) Wet season (<35 ppbv), (b) Dry season (30-70 ppbv) and (c) Dry season (>70 ppbv)

Precision of the developed sampling device, reported as the percent difference (%D) between duplicate pairs of samplers from two different methods. Table 3.4 shows %D of hourly ozone concentrations obtained from the developed AOSD with reference values from the AQM under optimum conditions. It was found that most of the values were less than 30%.

Table 3.4 Percent difference of 1-hr ozone concentrations obtained from the developed AOSD with reference values from the AQM in different seasons

Wet season (<35 ppbv)			**Dry season**					
			(30-70 ppbv)			**(>70 ppbv)**		
Ozone conc. (ppbv)		%D	Ozone conc. (ppbv)		%D	Ozone conc. (ppbv)		%D
AOSD	AQM		AOSD	AQM		AOSD	AQM	
22	27	-22%	42	33	25%	51	58	-13%
23	30	-26%	52	50	3%	60	71	-17%
19	23	-22%	61	64	-5%	79	77	3%
21	18	17%	48	58	-19%	74	68	9%
18	20	-13%	47	39	18%	56	88	-44%
25	23	8%	46	47	-2%	89	93	-4%
20	17	15%	60	45	28%	81	80	1%
14	11	27%	42	47	-11%	77	63	20%
23	28	-20%	35	41	-17%	70	69	1%
25	33	-27%	40	56	-34%	81	76	6%
22	20	9%	79	68	15%	73	82	-12%
17	17	1%	47	63	-30%	75	60	22%
16	16	3%	36	39	-8%	91	74	21%
23	28	-18%	51	47	9%	105	80	27%
19	16	18%	61	56	9%	82	68	18%
14	11	21%	45	53	-16%	62	56	10%
			37	34	9%	69	61	13%
			49	43	13%	82	73	12%
			55	54	2%	83	70	17%
			42	54	-24%	52	60	-15%
			45	35	26%	51	64	-23%
			49	42	16%	59	57	4%
			64	63	1%	62	51	19%
			52	65	-22%			

Refer to Table 3.4, number of measured values, which were over or under the reference values, were counted. Table 3.5 shows number of the measurement, which are over or under the reference values comparing with the AQM values. It was found that number of samples that over and under the reference values were almost equal both in wet and dry seasons with medium ozone concentrations. However, in dry season with high ozone concentrations, it was found that number of samples, which was over the reference values, was higher than those with under the reference values.

Table 3.5 Summary of over/under values of samplers from the developed AOSD compared with the reference values

Seasons	**Total samples (n)**	**Over the references**		**Under the references**	
		n	**%**	**n**	**%**
Wet (<35 ppbv)	16	9	56	7	44
Dry (30-70 ppbv)	24	13	54	11	46
Dry (>70 ppbv)	23	16	70	7	30

3.4 The relationships between ozone concentrations and meteorological conditions

Ozone concentrations obtained from the developed AOSD both in wet season with low ozone concentrations (n = 16) and dry season with medium ozone concentrations (n = 24) and high ozone concentrations (n = 24) were analyzed for correlations with meteorological parameters i.e. solar radiation (SR), net radiation (NR), temperature (Temp.), wind speed (WS), wind direction (WD), relative humidity (RH), pressure and rain. Meteorological data was obtained from the same AQM station. Their correlations are shown in Table 3.6.

Table 3.6 Correlations between ozone concentrations and meteorological parameters

Ozone concentrations	WS (m/s)	WD (m/s)	RH (%)	Temp. (°C)	SR (w/m^2)	NR (w/m^2)	Pressure (mmHg)	Rain (mm)
Low (<35 ppbv)	-0.166	-0.215	-0.186	0.187	0.407	**0.562***	**0.563***	-0.292
Medium [a] (30-70 ppbv)	-0.566	-0.098	-0.521	0.472	**0.702***	-0.243	-0.366	0.101
Medium [b] (30-70 ppbv)	0.231	-0.261	-0.086	**0.586***	**0.764****	**0.802****	-0.064	-0.306
High [c] (>70 ppbv)	-0.189	-0.433	-0.278	**0.667***	**0.587***	**0.738****	**-0.703***	-
High [d] (>70 ppbv)	-0.131	0.303	**-0.600***	**0.639***	0.327	0.266	-0.109	-

[a] Ozone concentrations in dry season with medium ozone concentrations (morning samples),

[b] Ozone concentrations in dry season with medium ozone concentrations (afternoon samples),

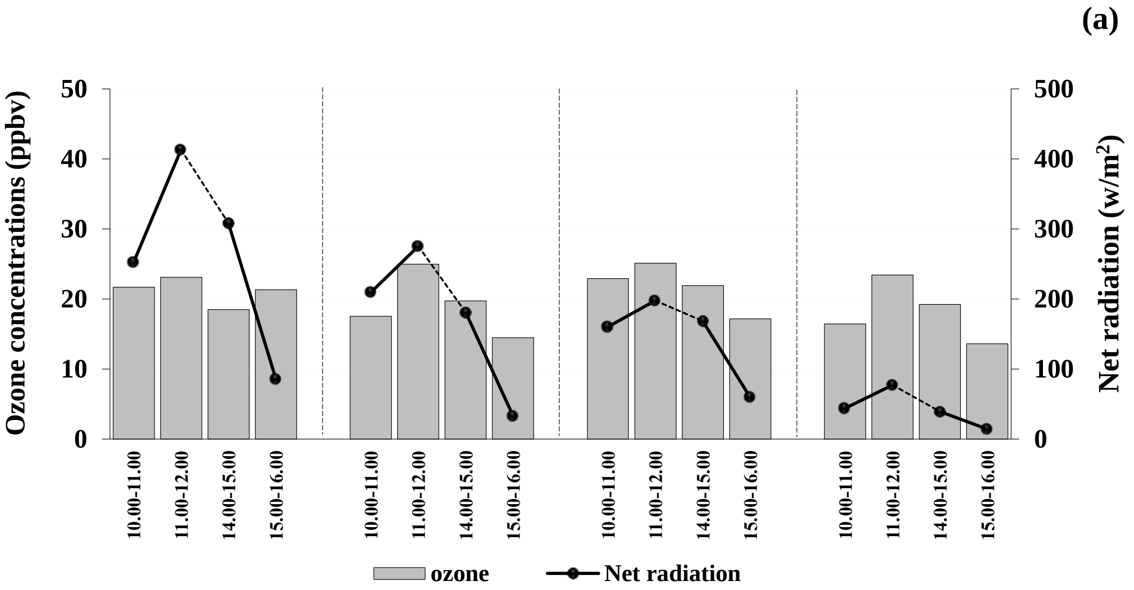
[c] Ozone concentrations in dry season with higher ozone concentrations (morning samples),

[d] Ozone concentrations in dry season with higher ozone concentrations (afternoon samples)

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

In wet season, the marine air mass from the Indian Ocean (the southwest monsoon) prevails over this region. As a result, precipitation, occasionally heavy rainfall, and high humidity throughout the country in this season (Pochanart *et al*, 2001). These are related to low pressure systems. The weather is often wet and windy (Hüseyin *et al*., 2005). Moreover, the non-availability of adequate solar radiation due to the cloudy skies that reflected back the solar radiation from reaching the surface (Elampari *et al*., 2001). Therefore, considering the relationship between ambient ozone concentrations in wet season and meteorological parameters (n = 16), it was found that ozone concentrations were well correlated with net radiation (r = 0.562) and pressure (r = 0.563) as shown in Figure 3.8. Figure 3.9 shows the patterns of ozone concentrations from AOSD and AQM, net radiation and pressure. It was found that ozone concentrations from both methods showed the same trend with net radiation and pressure.



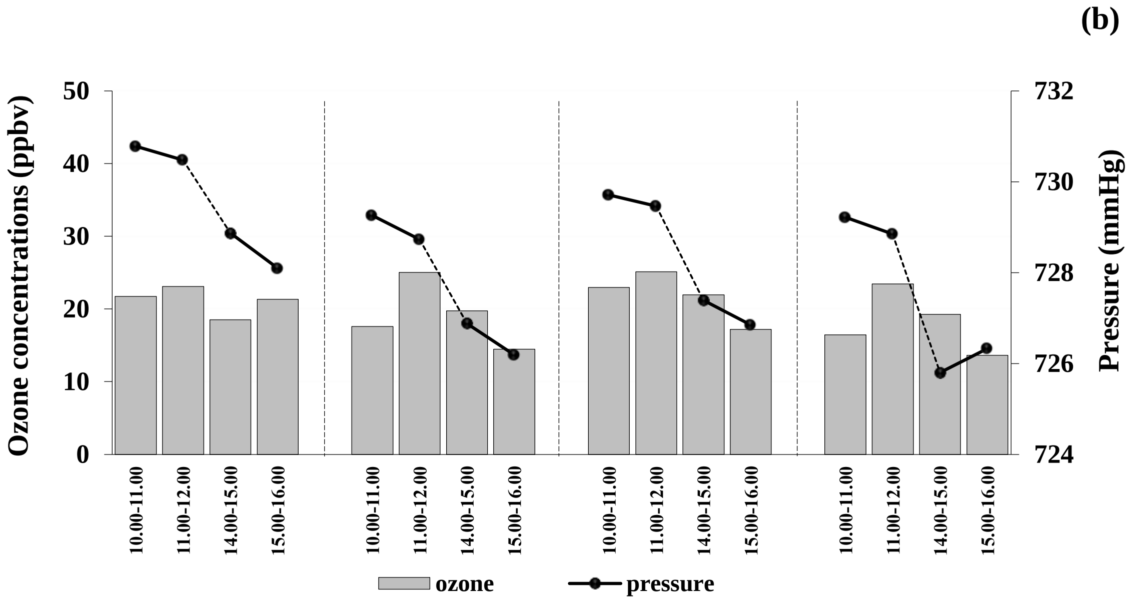


Figure 3.8 Relationships of ozone concentrations with (a) Net radiation and (b) Pressure in wet season with low ozone concentrations

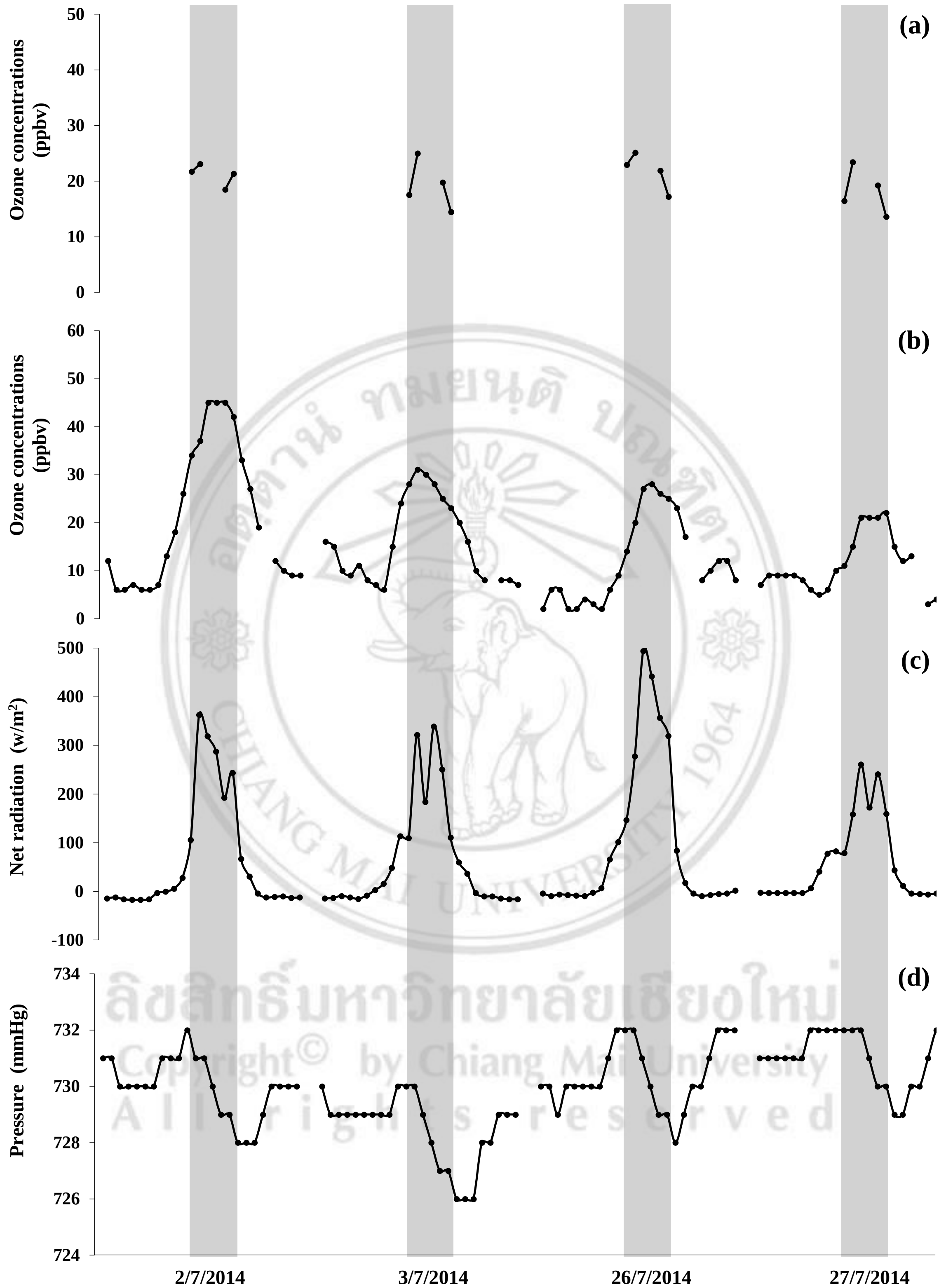


Figure 3.9 Patterns of parameters in wet season (a) ozone concentrations from AOSD, (b) ozone concentrations from AQM, (c) net radiation and (d) pressure

In dry season with medium ozone concentrations (cool dry season) usually starts in November with the shift of the southwest monsoon to the northeast monsoon (winter monsoon) which brings the continental air mass from the northern or northeastern part of the Asian continent and the ends in late-February (Pochanart *et al*., 2001). According to Thai Meteorological Department, the Upper Thailand was less rain and to become cool or cold in the morning while warmer air occurs with hot air during day time. The higher temperature and solar radiation intensity during mid-day time lead to increasing in the photochemical reactions (Khoder *et al*., 2009). Therefore, considering of the relationship between ambient ozone concentrations in dry season with medium concentrations (30-70 ppbv) and meteorological parameters was found that all samplers (n = 24) were well correlated with solar radiation (r = 0.764). However, only the samples taken in the afternoon period were well correlated with net radiation (r = 0.802) and temperature (r = 0.586) as shown in Figure 3.10. The ozone sampling was conducted for 1 hour in December, which is cool and foggy in the early morning while it is hot and dry in the afternoon. There was a great variation of temperature and net radiation values as well as ozone concentrations from morning to afternoon periods in dry season. The pattern of ozone concentrations from both methods as well as solar radiation, net radiation and temperature values are shown in Figure 3.11. It was found that all of parameters showed the same trend during sampling period.

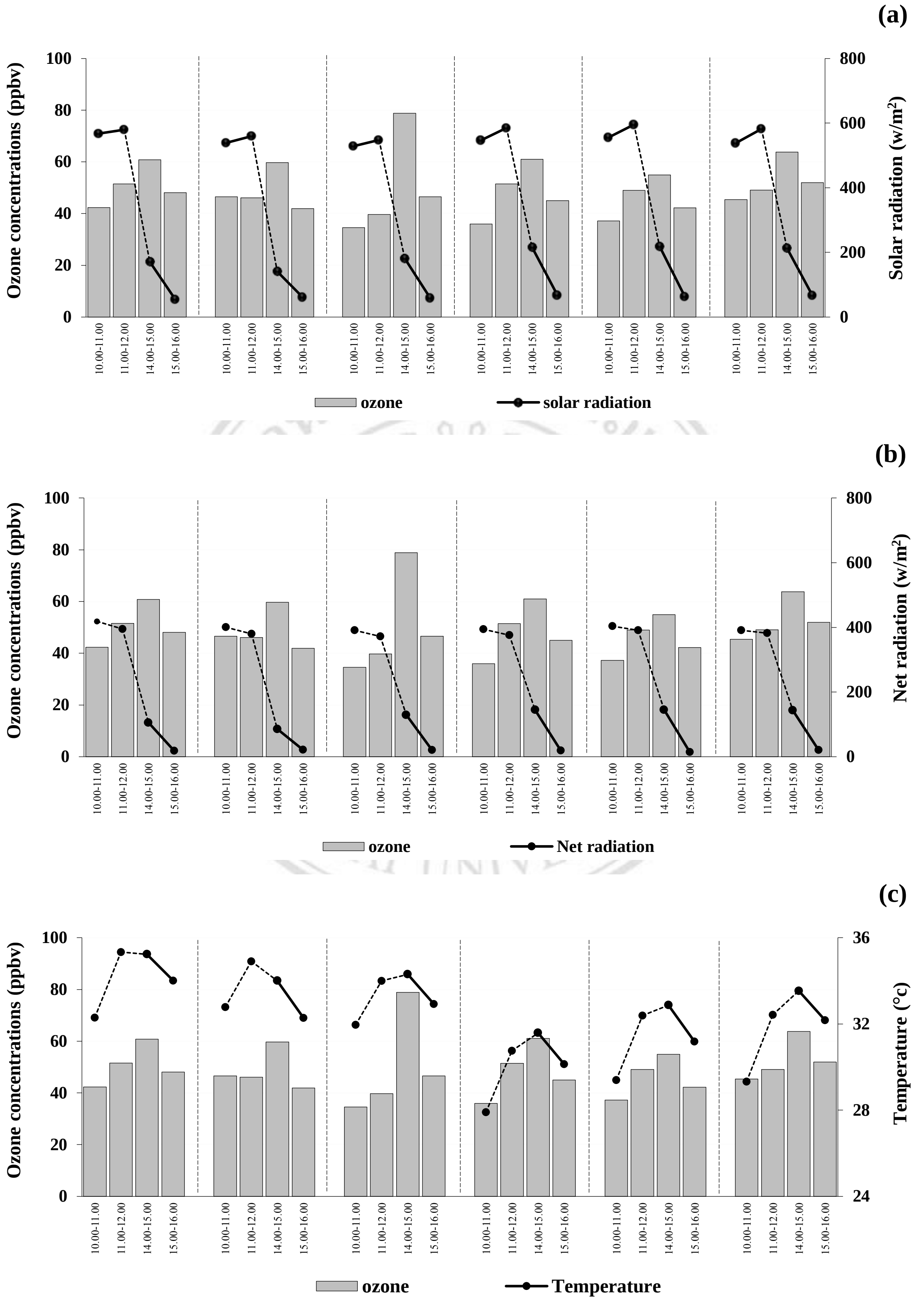


Figure 3.10 Relationships of ozone concentrations with (a) Solar radiation, (b) Net radiation and (c) Temperature in dry season with medium ozone concentrations

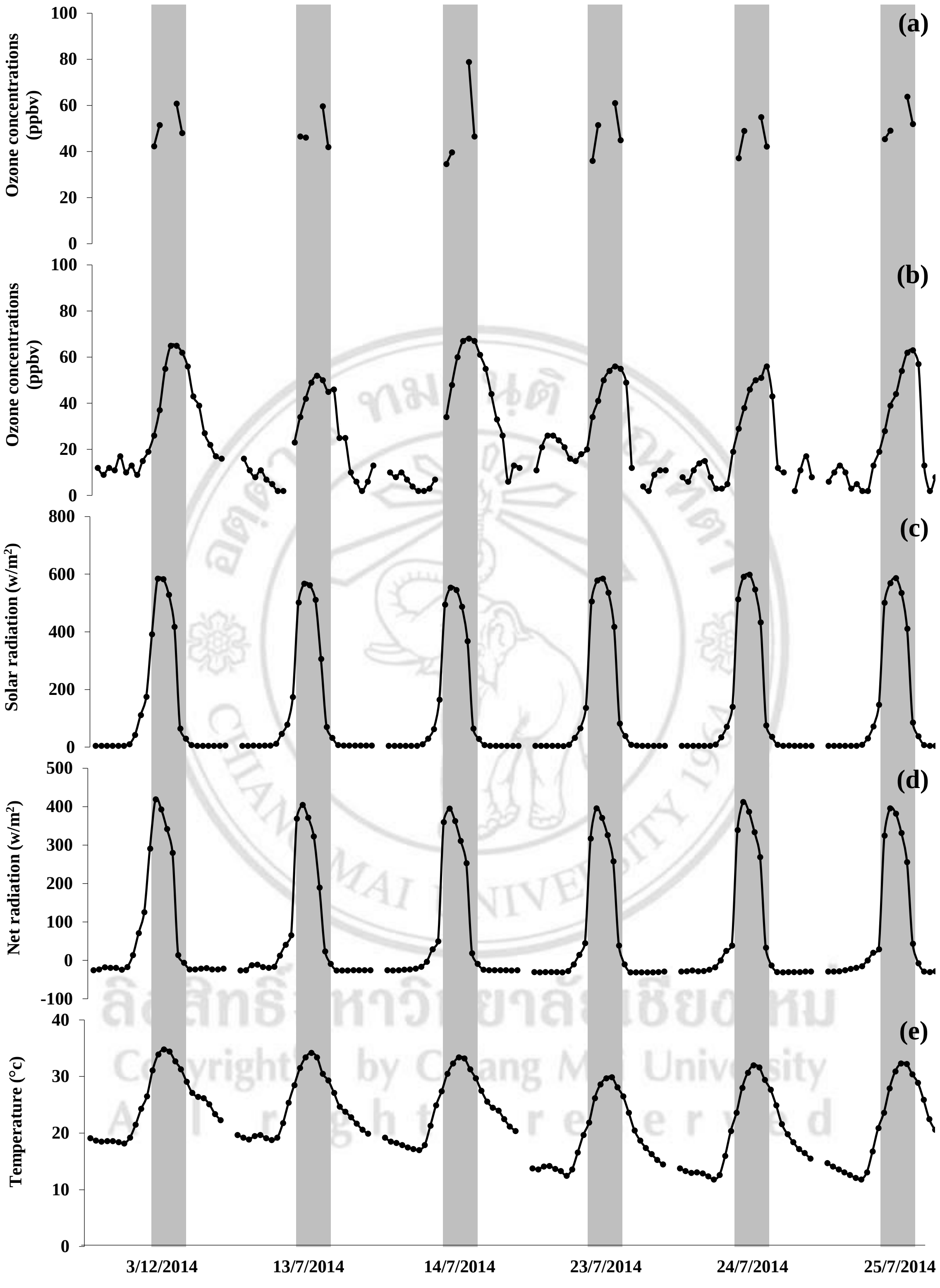
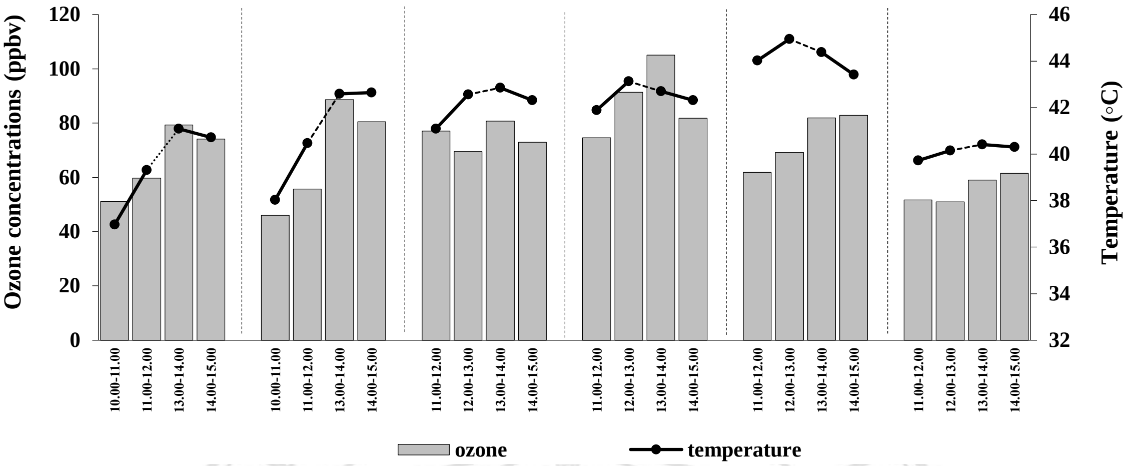


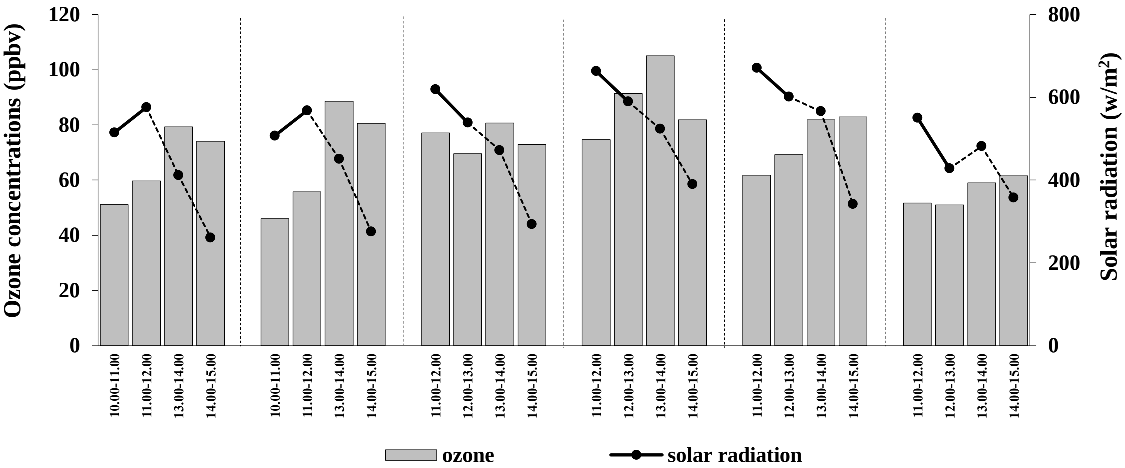
Figure 3.11 Patterns of parameters in dry season with medium ozone concentrations (a) ozone concentrations from AOSD, (b) ozone concentrations from AQM, (c) solar radiation, (d) net radiation and (e) temperature

In dry season with high ozone concentrations (hot dry season) usually begin in March - May, which the extremely hot due to the strong solar intensity and the localized low-pressure zone (Pochanart *et al*., 2001). Especially in March and April are known as local summer in Thailand. During summertime ozone concentrations increase during periods of the higher solar radiation intensity and temperature (Zhang *et al*., 1998), which 67% of the variation of ozone concentrations during the summer could be accounted for by changes in temperature and solar radiation (Kovač *et al*., 2009). These parameters can directly enhance ozone concentrations by affecting ozone formation as well as ozone precursor emission rates (Ooka *et al*., 2011). Moreover, it found that peak ozone concentrations typically occur in the early afternoon, shortly after solar noon when the sun's rays are most intense. In contrast, the highest average concentration for ozone occurred at relative humidity less than or equal to 40% (Elminir *et al*., 2005), which found that 70% of the day-to-day ozone variability could be explained by changes in temperature and relative humidity (Tarasova *et al*., 2003). Relative humidity can be mainly attributed to the enhanced oxidation of hydrocarbons in the afternoon, which support the ozone production (Elminir *et al*., 2005; Tu *et al*., 2007). Therefore, considering the relationship between ambient ozone concentrations in dry season with high concentrations (>70 ppbv) and meteorological parameters was found that all samplers (n = 24) were well correlated with temperature (r = 0.667), solar radiation (r = 0.587), net radiation (r = 0.738) and pressure (r = -0.703) but only the sampler taken in the morning period. While the sampler taken in the afternoon period were well correlated with temperature (r = 0.639) and relative humidity (r = -0.600) as shown in Figure 3.12. This is probably due to the great variation of solar radiation and occurrence of wind in afternoon period. Solar radiations are most intense at noon and keep decreasing after noon, while temperature increased (maximum ~2-3 pm.) and relative humidity decreased (minimum ~2-3 pm.). Generally ozone increasing with increasing temperature and decreasing relative humidity (Camalier *et al*., 2007). The similar patterns are found in this study as shown in Figure 3.13. Beside, occurrence of wind in afternoon period are affecting accumulation of precursors of ozone formation (VOCs and NOx) and the subsequent formation of ozone in ambient. So, peak ozone concentrations typically occur in the early afternoon, which is correlated with temperature and relative humidity. The pattern of relationship between ozone concentrations, solar radiation, net radiation, temperature, pressure and relative humidity are showed in Figure 3.13.

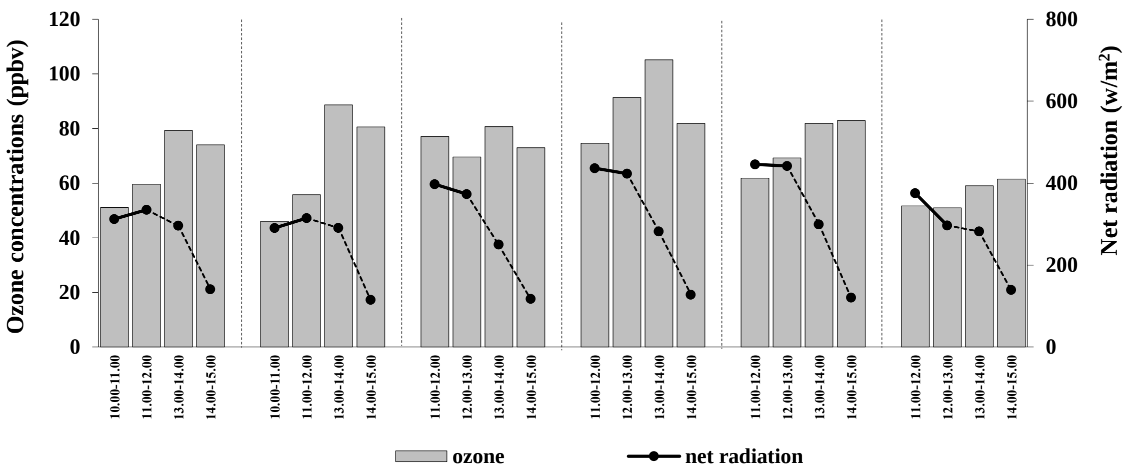
(a)



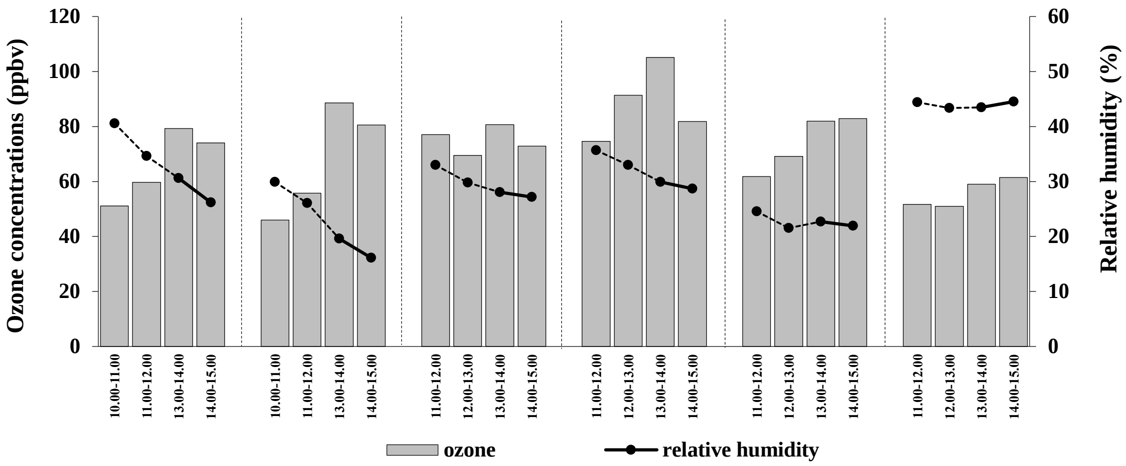
(b)



(c)



(d)



(e)

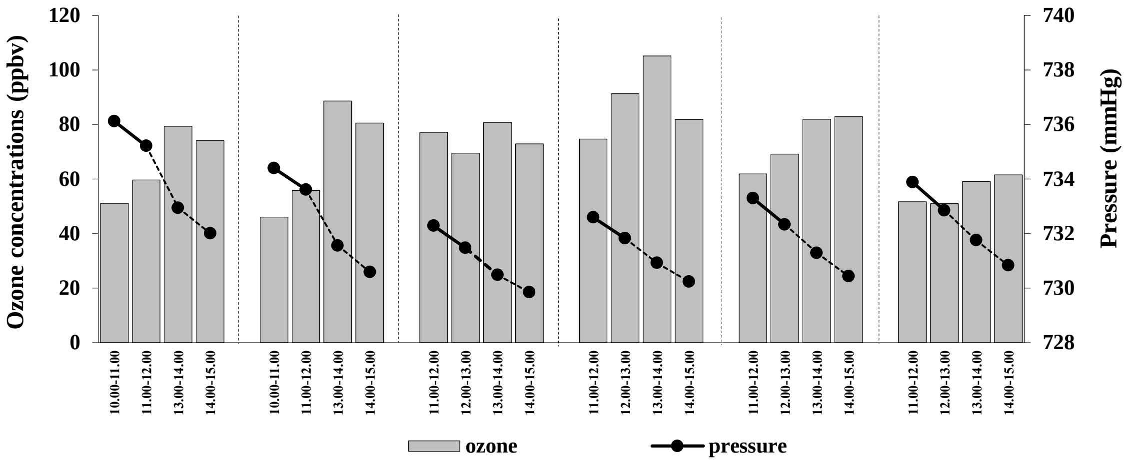


Figure 3.12 Relationships of ozone concentrations with (a) Temperature, (b) Solar radiation, (c) Net radiation, (d) Pressure and (e) Relative humidity in dry season with high ozone concentrations

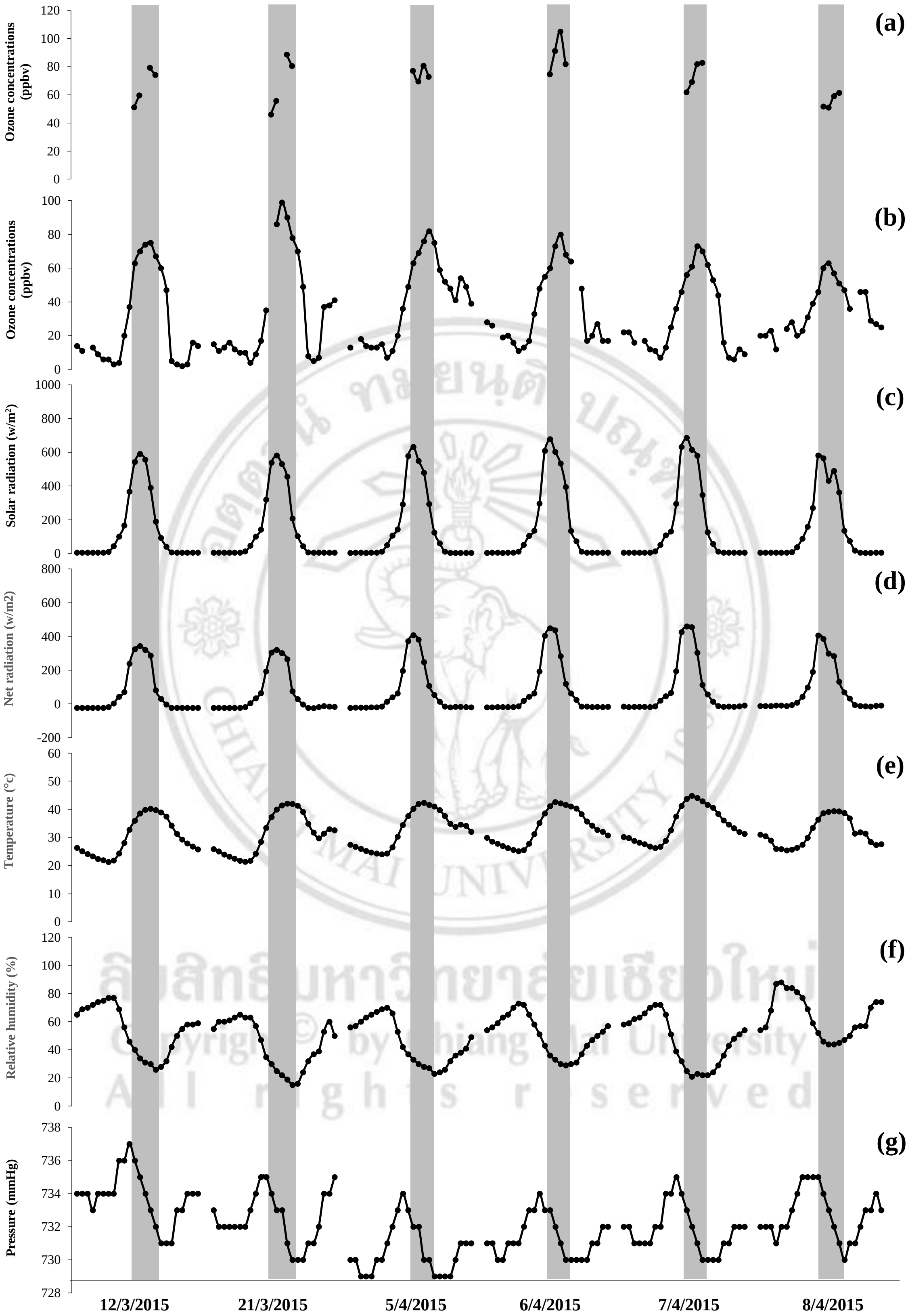


Figure 3.13 Patterns of parameters in dry season with high ozone concentrations; (a) ozone concentrations from AOSD, (b) ozone concentrations from AQM, (c) solar radiation, (d) net radiation, (e) temperature, (f) relative humidity and (g) pressure

3.5 Limit of Detection (LOD) of Ion chromatography for nitrate measurement

According to Taylor (1987), LOD value was calculated as three times of standard deviation (SD) of the noise at zero solution. Their concentrations were calculated from the calibration curve in ranges of 0.05 to 1.00 µg/ml of NO_3^- standard (r^2 = 0.9996). LOD values of all analytes are shown in Table 3.7.

Table 3.7 Limit of detection of IC (Metrohm)

NO. of injection	concentration of NO_3^- (µg/ml)
1	0.054
2	0.058
3	0.053
4	0.056
5	0.057
average	0.0557
standard Deviation (SD)	0.0023
Limit of detection (3xSD)	**0.0069**
Limit of Quantification (10xSD)	0.0231

3.6 Limit of detection limit of active sampling method for ozone

The limit of detection of method collected by the active sampling device, can be calculated according to Geyh et al., 1997.

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

The standard deviation of nitrate concentrations of test blank ($\sigma_{NO_3^-}$) from each optimum condition were calculated from the calibration curve in ranges of 0.05 to 1.00 µg/ml of NO_3^- standard (r^2 = 1).

SD values of blank are shown in Table 3.8 and LOD of active sampling method are shown in Table 3.9.

Table 3.8 Standard deviation of nitrate concentrations of test blank

NO. of blank	**concentration of NO_3^- (µg/ml)**		
	(1)	**(2)**	**(3)**
1	0.066	0.082	0.175
2	0.065	0.081	0.151
3	0.068	0.090	0.145
4	0.066	0.115	0.155
5	0.071	0.108	0.157
6	0.071	0.128	0.154
7	0.077	0.130	0.207
8	0.081	0.130	0.160
9	0.073	0.120	0.206
average	0.071	0.109	0.168
standard Deviation (SD)	**0.005**	**0.020**	**0.023**

** (1) = the optimum condition for ozone sampling in wet season with low concentrations (0.5%$NaNO_2$/0.5%Na_2CO_3/5%ethylene glycol + 1.2 L/min)

(2) = the optimum condition for ozone sampling in dry season with medium concentrations (0.75%$NaNO_2$/0.75%Na_2CO_3/7.5%ethylene glycol + 0.5 L/min)

(3) = the optimum condition for ozone sampling in dry season with higher concentrations (1.25%$NaNO_2$/1.25%Na_2CO_3/12.5%ethylene glycol + 0.5 L/min)

Table 3.9 Limit of detection of active sampling method

Season	**Absorbing solution**			**Air flow rate (L/min)**	**LOD (ppbv·h)**
	$NaNO_2$ (%w/v)	**Na_2CO_3 (%w/v)**	**Ethylene glycol (%v/v)**		
Wet (<35 ppbv)	0.50	0.50	5.0	1.2	**0.87**
Dry (30-70 ppbv)	0.75	0.75	7.5	0.5	**7.89**
Dry (>70 ppbv)	1.25	1.25	12.5	0.5	**9.20**