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Photochemical smog pollution in the Bangkok Metropolitan Region of Thailand in relation to O_3 precursor concentrations and meteorological conditions

B.-N. Zhang, N.T. Kim Oanh*

Environmental Engineering, SERD, Asian Institute of Technology, P.O. Box 4, Klong Luang, Pathumthani 12120, Thailand

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Abstract

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

Keywords: Photochemical pollution; Meteorology; Precursors; Bangkok

1. Introduction

Photochemical smog, first identified in Los Angeles in the late 1940s, nowadays is a widespread phenomenon in many of the world's population centers (Jenkin and Clemitshaw, 2000). Ozone, the main oxidant in photochemical smog, is known to have adverse effects on human health, vegetation and materials.

Formation/destruction and accumulation of ozone in urban polluted areas are complex phenomena that involve physical and chemical processes in the lower troposphere and exchange air with stratosphere. As a secondary pollutant, ozone is not emitted directly into the atmosphere but formed as the photochemical reaction product of the precursors, VOC and NO_x, in the presence of sunlight. In the atmosphere O_3 and its precursors undergo the transport, turbulent diffusion, wet and dry deposition, which are mostly determined by meteorological conditions. Local meteorological conditions such as solar radiation, temperature, and cloud cover affect the rates of photochemical reactions and biogenic VOC emission. Rainy conditions, for example, are normally associated with low O_3 level (Ghim et al.,

*Corresponding author.
E-mail address: kimoanh@ait.ac.th (N.T. Kim Oanh).

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2001). Other meteorological parameters such as wind speed and mixing height determine dispersion of O_3 and the precursors in the boundary layer. Meteorology also determines the regional transport of ozone and its precursors to the area as well as the intrusion of O_3 from upper layer to the boundary layer (Pochanart et al., 2001; Chan et al., 1998a). The relationship between precursor pollutants and ozone, thus, differs from one place to another due to the emission distribution and meteorology (NRC, 1991).

In tropical region high ozone level may be expected due to high rate of precursors emission from both anthropogenic and biogenic sources coupled with the high sunlight intensity. Yet there is only a limited research for tropical tropospheric ozone that has been conducted for Asia (Pochanart et al., 2001; Lal et al., 2000; Chan et al., 1998a, b). The lack of systematic monitoring data of ozone and its precursors is one of the barriers to the scientific research for photochemical smog in most of the developing Asian countries.

This paper describes the O_3 pollution status and trend in Bangkok Metropolitan Region of Thailand in recent years, 1996–2000. Average monthly and diurnal variations of ozone are analyzed in connection with variations of O_3 precursors and meteorological conditions. Observational data are used to estimate the effective NO_x/NMHC ratio for production of O_3, and seasonal variations in NO_x/NMHC ratios are analyzed to assess the seasonal photochemical smog potentials. This work is a part of a study for photochemical smog modeling for Bangkok city conducted at the Asian Institute of Technology, Bangkok, Thailand.

2. Study area and data collection

Climate in Thailand varies seasonally according to the typical monsoon regime, only two major seasons are identified. The rainy (wet) season starts from 16 May and ends on 15 October. Precipitation and high humidity are common throughout the country in this season. The dry season can be subsequently classified into two periods. The first period, from 16 October to 15 February, is characterized by a mild weather of the winter monsoon, which is referred to as winter. The second period is known as local summer in Thailand, from 16 February to 15 May, which is extremely hot (Ostro et al., 1999; Pochanart et al., 2001).

Bangkok, the capital of Thailand, is located on an open plain. The plain is the alluvial basin of the Chao Praya river that enters the Gulf of Thailand at Samut Prakarn, to the south of Bangkok. Bangkok has the registered population of over 5.6 million in December 1998. The area of Bangkok is of 1570 km^2 with the population density of around 3500 people km^{-2} (BMA, 1999). The Bangkok Metropolitan Region, BMR, includes Bangkok and five surrounding provinces, namely Samut Prakarn, Nonthaburi, Pathumthani, Nakhon Pathom, and Samut Sakhon. They are closely linked in terms of traffic and industrial development.

Bangkok has experienced serious air pollution problem that is largely due to high emission from mobile sources with high vehicle kilometer traveled and high traffic congestion (Supat, 1999a). The vehicular emission in the Bangkok city contributed 62% of NO_x, 71% of CO and 73% of VOC of the total vehicular emission in the BMR (Table 1). In spite of measures taken in the emission control and management, air quality is not obviously improved (Supat, 1999a). In 2000 many pollutants were still found exceeding the national air quality standards at curbside stations such as 1 and 8 h CO (0.01–0.02% of measurements) and 24 h TSP (5.9%), 24 h PM10 (12.8%), and at general ambient stations 1 h O_3 (0.3%) and 24 h PM10 (2.1%) (PCD, 2001).

The data used for this study were collected from the Pollution Control Department (PCD) in Bangkok, comprising of data from 13 continuous automatic ambient air quality monitoring stations in Bangkok and 5 stations in the provinces of BMR at which ozone data are available (Fig. 1). The stations in Bangkok are divided into two categories, the general ambient air quality monitoring stations that are located within 50–100 m from main road (stations 1–10, Fig. 1), and the curbside street-level ambient air quality monitoring stations that are within 2–5 m from main road (stations 11–13). General ambient stations are placed in residential, commercial, industrial, and mixed areas of Bangkok (Supat, 1999b).

All monitoring stations are operated automatically with remote control from the central computers located at the PCD. The stations are equipped to monitor CO, TSP, PM10, Pb, SO_2, NO_x, O_3, CH_4 and NMHC. For Bangkok stations, stations 1–5 have started operation since January 1996 while the rest started operation since

Table 1
Pollutant emission rates (t yr^{-1}) for Bangkok and other provinces in BMR in 1997

Area	Source	NO_x	CO	VOC
Bangkok	Point	6553	909	382
	Mobile	164,737	249,320	171,086
	Area	6434	4467	8468
	Subtotal	177,724	254,696	179,936
Surrounding provinces	Point	49,449	5356	1623
	Mobile	99,911	100,451	61,888
	Area	2078	103,271	25,436
	Subtotal	151,438	209,078	88,947
Total for BMR		329,162	463,774	268,883

Source: PCD (2000).

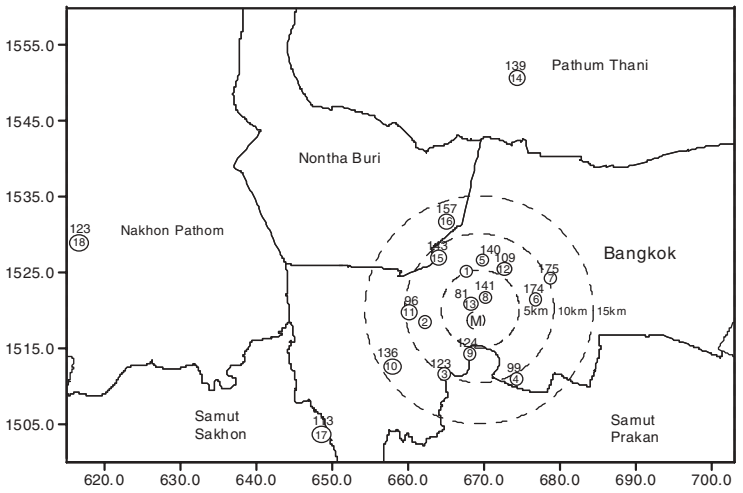


Fig. 1. Locations for air quality monitoring stations (circle and number) and meteorological station (M) in the UTM coordinate system (km). The values indicate the average of yearly highest maximum of hourly O_3, in ppbv, during 1998–2000. Monitoring stations: 1 OEEP, 2 Bansomdat, 3 Ratburana, 4 Met. Dept., 5 Junkasame, 6 Ramkhamhaeng, 7 National Housing, 8 Huaikhwang, 9 Nonetree, 10 Singha, 11 Thonburi, 12 Traffic Police, 13 Dindang, 14 Rangsit, 15 Energy Affairs, 16 Nonthaburi, 17 Thonaburi Highway and 18 Sanamchan.

September 1996. Exceptions are stations 1 and 2 where no O_3, CH_4, and NMHC are monitored, and station 3 where no CH_4 and NMHC are monitored. Thus, totally only 11 stations in Bangkok have O_3 monitoring data. Besides, O_3 data are available at No. 14 since January 1996 and at stations 15–18 since September 1996.

The measurement equipment includes API 400 Ozone Analyzer for ozone; Gas Filter Correlation CO Analyzer API Model 300 for CO; API Model 200 Analyzer for $NO/NO_2/NO_x$; and APHA-360 Ambient THC Monitor for NMHC and CH_4. Automatic zero and span checks of gas analyzers in the stations are performed daily and manual calibrations with standard gases of USEPA protocol grade are made every 15 days to ensure good data quality (Supat, 1999b).

There are 2 international meteorological stations located in Bangkok: the Bangkok Metropolis located in the city center (Fig. 1), and the Donmuang airport on the city periphery. In this study hourly meteorological data collected at the Bangkok Metropolis station were used. This station is equipped with a wind vane of 33 m height above the ground so as to reduce the surrounding obstruction effects.

3. Results and discussion

3.1. Status and trend of ozone pollution in BMR

Highlights of O_3 pollution status in the BMR are presented in Table 2. In general, the ambient stations in Bangkok had higher maximum O_3 levels as well as higher frequency (hours) of exceeding Thai NAAQS for O_3 (100 ppbv) than stations in the surrounding provinces.

The limited monitoring data available are not evenly distributed over the study area, which makes a careful assessment of spatial distribution of O_3 difficult. Assuming the city center point to be located in the old part of the city, at the intersection of Asoke and Petchburi roads, which are generally characterized by dense population and traffic roads, the inner 5 km circle surrounding the point is represented by lower hourly maximum O_3 (Fig. 1). Curbside station 13, also located inside the 5 km circle, always has lowest O_3 level and never exceeded 100 ppbv during the 5-yr period. Curbside stations 11 and 12, located within 10 km circle, are characterized by lower frequency of O_3 exceeding standards than ambient stations, i.e. 1 h at station 11 and 11 h at station 12 for the 5-yr period (Table 2).

Among the ambient monitoring stations, station 8, located closest to the city center point, 1.6 km, is characterized by the lowest number of hours exceeding the standard during the study period, 7.5 h yr^{-1}. Highest maximum hourly O_3 levels were observed at station 5, 370 ppbv, followed by Nos. 6, 4 and 7 (Fig. 1). However, the frequent missing data at station 4 (19 months missing in 1999–2000) and station 5 (18 months missing in 1998–1999) during the 5-yr period may be the reason for the relatively low annual averages of hours exceeding 100 ppbv presented in Table 2. Frequency of O_3 exceeding the standard in Bangkok is highest at station

Table 2
Summary of O_3 pollution exceeding the Thailand National Air Quality Standard (100 ppbv) from 1996 to 2000

Station	1996[a]			1997			1998			1999			2000			Total hours	Average hours ($h\,yr^{-1}$)[b]
	Total hours	Total days	Max. O_3 (ppbv)	Total hours	Total days	Max. O_3 (ppbv)	Total hours	Total days	Max. O_3 (ppbv)	Total hours	Total days	Max. O_3 (ppbv)	Total hours	Total days	Max. O_3 (ppbv)		
3	2	1	127	28	8	180	4	2	132	1	1	102	26	12	136	61	14.8
4	12	10	174	33	18	221	0			0[c]			0[c]			45	15
5	20	14	172	8	6	370	0[c]			4[c]	2	126	10	7	153	42	12.7
6	0			26	17	148	56	23	166	31	14	152	51	23	203	164	41
7	0			19	13	124	39	16	191	12	6	141	24	14	193	94	23.5
8	1	1	100	8	5	190	9	5	122	4	4	157	9	5	143	31	7.5
9	1	1	104	20	9	141	7	6	136	5	3	109	12	5	127	45	11
10	1	1	115	43	17	181	16	7	154	4	2	115	37	14	139	101	25
11	0			0			1	1	101	0[c]			0			1	0.3
12	0			4	3	114	2	2	112	0			5	3	136	11	2.8
14	3	2	112	41	26	167	0[c]			2	1	131	11	7	146	57	14.3
15	0			15	7	141	7	4	127	10	6	127	27	12	174	59	14.8
16	7	7	149	43	20	168	30	14	157	0[c]			0[c]			80	36.5
17	0			17	8	186	1[c]	1	100	8	6	112	19[c]	9	127	45	11.3
18	0			9	6	121	13	5	127	3[c]	1	115	11	4	126	36	9
Total	47			314			185			84			242				

[a] Ozone monitoring at Nos. 4, 5 and 14 started from January 1996, at other stations started from September 1996.

[b] Calculated based on available database. No. 4 based on the 3 years 1996–1998, No. 5 on the 3 years 1996–1997 and 2000, No. 14 on the 4 years 1996–1997 and 1999–2000, No. 16 on the 2 years 1997–1998, other stations on the 4 years 1997–2000.

[c] Missing data.

Station 4: May–December 1999, January–May and July–December 2000.

Station 5: January–May and August–December 1998, January and April–October 1999.

Station 11: January–February and May–June 1999.

Station 14: January–August 1998.

Station 16: March–December 1999 and January–October 2000.

Station 17: November–December 1998 and May–July 2000.

Station 18: May–September 1999.

6 (7.6 km from the center point), 41 h yr^{-1}, second at station 10 (14 km), 25 h yr^{-1}, which is followed by station 7 (10 km), 23.5 h yr^{-1}. In the other provinces of BMR the frequency of exceeding standard is high at station 16, 36.5 h yr^{-1}, followed by stations 14 and 15, 14–15 h yr^{-1}.

High emission of NO from traffic should be the major reason for low O_3 at the curbside stations and lower O_3 at ambient station 8 (Fig. 1 and Table 2). This is the result of O_3 destruction by NO in the nitrogen dioxide photolytic cycle, which is effective at a close distance to NO sources due to its short cycle time, about several minutes (Jenkin and Clemitshaw, 2000). The high O_3 observed at stations located at a distance from the city center reflect the dispersion of O_3 and its precursors, and photochemistry associated with the longer time cycle of conversion from NO to NO_2, involving reactive hydrocarbons and the OH radical about several hours (Seinfeld and Pandis, 1998).

It is worth noting that in a city like Bangkok where the emission of NO from traffic is rather uniformly spread over a large area the processes of O_3 destruction (by NO) and formation should be competing at any location. Therefore O_3 level is found to be high over the city except for the very heavy traffic city center and curbside where the O_3 destruction by NO is significant. High level of O_3 in the surrounding provinces should be the result of transport of O_3 and precursors from Bangkok, regional transport as well as the emission of O_3 precursors from these provinces.

Fig. 2 presents the change of O_3 pollution in Bangkok from 1996 to 2000, averaged for 8 general ambient stations (Nos. 3–10) where O_3 data are available. It is noted that the data for 1996 was available only for 4 months September–December for most of the stations and hence 1996 was not included in the following discussion. 1997 was characterized by the highest total hours exceeding standard from all stations in BMR, 314 h, and Bangkok, 185 h, as well as the maximum hourly O_3 concentration, 370 ppbv (Table 2). High ozone pollution observed in BMR in 1997 is most likely related to the ozone enhancement in Southeast Asia due to abnormal meteorology related to strong El Niño in the year and the forest fire in the region (Thompson et al., 2001).

Both average and 95 percentile values indicated a slight increase of O_3 since 1998 to 2000. The respective values for 2000 were 15.6 and 54 ppbv as compared to other years of 13.6–14.0 and 47–49 ppbv. The lowest average and 95 percentile were observed in 1998, 13.6 and 47 ppbv, respectively. Year 2000 also has a high number of hours exceeding 100 ppbv (second to 1997) in BMR, 242 h, and in Bangkok alone, 169 h. The O_3 increase trend in 1998–2000 is however not significant and there are uncertainties in attributing it to emission change due to the masking effects of year-to-year changes in meteorological conditions. The portion of variance in raw O_3 data explained by meteorological variables in the US, for example, was 20–60% depending on location (Wolff et al., 2001). It is however noted that there may be a change in emission of O_3 precursors in the study area related to the gasoline reformulation programs following the successful phasing out of leaded gasoline in Thailand in January 1996. Precautious measures had been taken to protect ambient air quality and public health including regulations on benzene content (<3.5% by volume, since January 1992), oxygen content of premium gasoline (1–2% by weight using methyl-tertiary-butyl-ether, since 1993). The new vehicles registered after 1993 have been reinforced to equip with catalytic converters and hence would reduce CO and HC substantially. However, there is still a large old in-use fleet (without emission control), which may be on Bangkok roads for the next 10–15 yr (Supat, 1999a). In this transitional period the CO, HC emission from vehicles is expected to be high. The emission is expected to reduce when the fleet turnovers and also after the regulation on the aromatic content come into effect (<35% by volume, since January 2000).

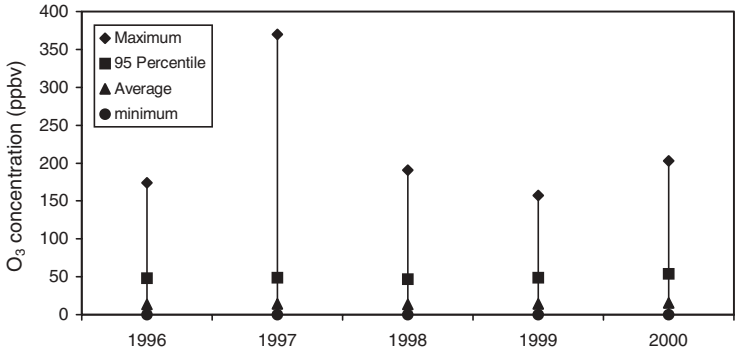


Fig. 2. Ozone pollution trend based on observations at 8 ambient stations of Bangkok.

3.2. Monthly frequency of O_3 exceeding the NAAQS

Monthly average of hours of O_3 exceeding 100 ppbv for 8 ambient stations in Bangkok is presented in Table 3. The values fluctuated from year to year. In 1999 the number of hours exceeding standards is the lowest. Higher frequency exceeding NAAQS was observed in the period from January to May and lowest frequency was observed in rainy season from June to September.

Stations 6, 7 and 10 with high O_3 level, and No. 8 with low O_3 were selected for a more in-depth analysis due to the complete data series, i.e. without missing data. Monthly average of hourly O_3 values at these stations also showed highest O_3 in dry season and lowest values in July–August (middle of rainy season) with a minimum in August (Fig. 3).

Pochanart et al. (2001), studied the O_3 variations at remote rural sites, Inthanog and Srinakarin, of Thailand in 1996–1998, found a similar seasonal pattern for both sites locating 450 km apart, i.e. minimum in mid-wet season (July–September) and maximum in dry season, February–April. The authors concluded that the obtained seasonal pattern reflects the long-range transport of air mass under the influence of the Asian monsoon. The August O_3 level was lowest in a year and it is around 9.3 ± 4 ppbv (average and 1 standard deviation, SD) for both sites. The August minimum level at stations 6, 7 and 10 in Bangkok are 13.4 ± 9.3, 11.1 ± 7.6, and 10.2 ± 5.2 ppbv, respectively, i.e. higher than the value at remote sites. It is however noted that there are certain overlaps in the ranges obtained (averages $\pm$ SD) and the O_3 fluctuation in terms of standard deviation is larger for Bangkok stations. For station 8, the August minimum was 5.8 ± 4.4 ppbv, i.e. lower than the average value observed at the remote sites. Given the much higher emission of precursors in Bangkok compared to the two remote sites, photochemical formation/destruction of O_3 in Bangkok is expected to have a more significant role than at the remote sites. Thus, photochemical production contributed to elevated minimum O_3 at stations 6, 7, and 10, and photochemical destruction lowered minimum at station 8 in August, as compared to that at the two remote sites.

The monthly average of hourly O_3 obtained by Pochanart et al. (2001) was highest in March for both remote sites. In Bangkok the monthly maximum occurred over the period from December to April, rather than a single maximum in March. It is interesting to note that the monthly maximums obtained at the selected stations in Bangkok were much lower than the March maximums at the 2 remote sites, which were around 45 ± 21 and 55 ± 13 ppbv. The highest monthly average O_3 of the selected 4 stations, which was observed at station 6, was also in March but only 25.2 ± 13.8 ppbv. The March values at stations 7, 8 and 10 are 18 ± 11.4, 11.5 ± 9.5 and 21.9 ± 13 ppbv. The relative variations of O_3 monthly maximum, i.e. the ratio between the standard deviation and average, at the Bangkok stations were higher than the remote sites. Also, the highest values at 1 remote site never exceeded 100 ppbv and at the other site only 2 times were recorded at 104–105 ppbv for the 2-yr observations as compared to the much higher frequency of exceeding standard in Bangkok (Table 2). The local meteorological conditions and emission sources in Bangkok are thought to contribute significantly to these high O_3 episodes and high fluctuations in O_3 levels. It is noted that the study period of Pochanart et al. (2001) was shorter than the present study, i.e. only 2 years including 1997 with the highest O_3.

Spring maximum and summer minimum tropospheric O_3 are commonly observed in many locations in the Northern hemisphere (Chan et al., 1998a; Saito et al.,

Table 3
Number of hours exceeding 100 ppbv from 8 ambient stations in Bangkok, from 1996 to 2000[a]

Month	1996	1997	1998	1999	2000	Total
January	2	43	43	4	15	107
February	7	12	18	4	17	58
March	2	27	1	13	65	108
April	4	28	7	8	20	67
May	3	20	22	5	9	59
June	2	3	2	0	3	10
July	1	0	18	5	0	24
August	1	2	8	0	1	12
September	2	15	1	1	6	25
October	2	18	1	7	5	33
November	3	14	1	5	11	34
December	8	3	9	9	17	46
Total	37	185	131	61	169	583

[a] Except for No. 4 and No. 5 stations, in 1996 only 4 months of data (September–December) are available.

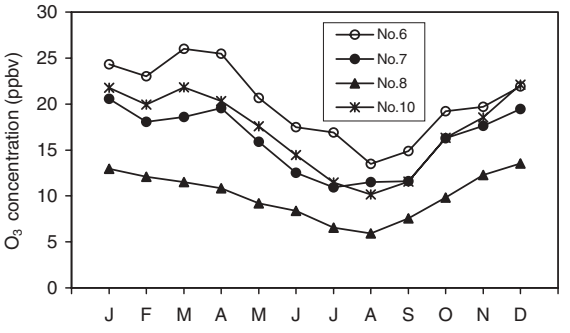


Fig. 3. Monthly ozone average values for the period 1996–2000.

2001). There are uncertainties in relating the maximum and minimum to natural and anthropogenic contributions (Saito et al., 2001). Degree of intrusion of stratospheric O_3 rich air to troposphere, local emission, as well as large-scale transport, are among the main causes. Chan et al. (1998b) noted that the long-range transport of oceanic and continental air masses associated with Asian monsoon is the governing factor for the temporal O_3 pattern in Hong Kong, and the stratosphere intrusion is not a dominant source of surface O_3 in Hong Kong. Saito et al. (2001) and Chan et al. (1998b) related the summer O_3 minimum in Japan and Hong Kong, respectively, to the inflow of the clean maritime tropic air mass. Bangkok is located at low latitude and intrusion of the stratospheric O_3, thus, is not expected to be significant. The high O_3 in the dry season in Bangkok may be caused by local emissions and meteorological conditions as well as the regional transport of O_3 and precursors from the Asian continent associated with the NE monsoon. Higher GR in March–April and temperature (average daily maximum of 34°C) and lower cloudness create favorable conditions for photochemical reactions. Wark et al. (1998) noted that a change of 40°F (about 4.4°C) would increase the overall rates of photochemical reactions by a factor of 2–4.

Low O_3 throughout the period of rainy season in BMR may be related to the inflow of maritime air mass. The lower O_3 from July to September with a minimum in August is most probably related to the more rain, higher cloudness, and lower solar radiation (Table 4). Rain could dramatically decrease O_3 and ended episodes observed in Seoul (Ghim et al., 2001), which was related to a number of causes including aqueous reactions in clouds consuming radicals or effects of vertical mixing, wet deposition of soluble O_3 precursors, decrease in solar radiation, and decrease in temperature.

3.3. Diurnal variation of ozone and its precursors

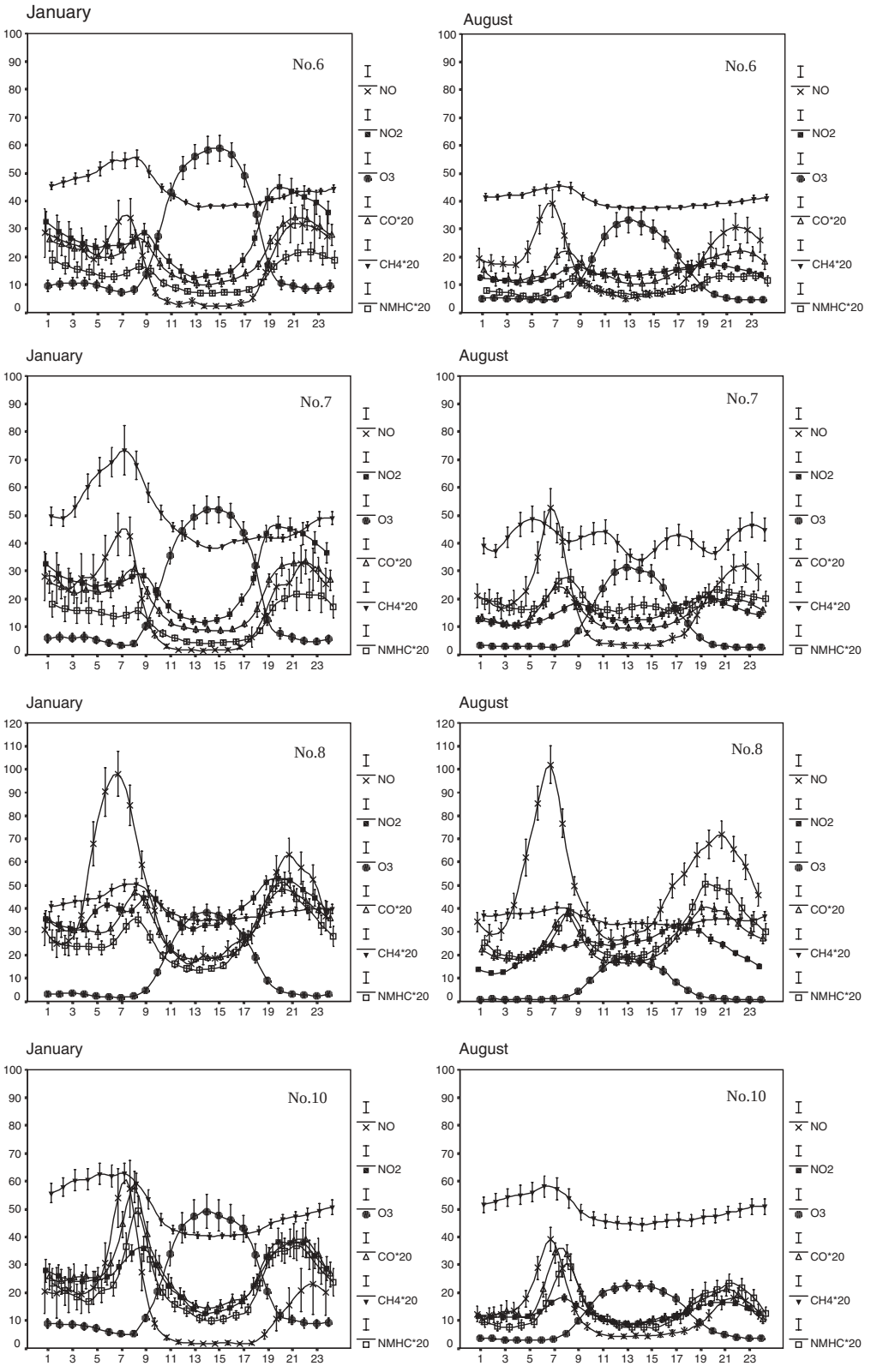
Diurnal variations of photochemical pollution precursors, NO, NO_2, CO, NMHC, and CH_4, and O_3 for the selected stations (6, 7, 8 and 10) for each month were analyzed. January (with high O_3) and August (with minimum O_3) data for the stations are presented in Fig. 4. Each point in Fig. 4 represents the average of up to 155 hourly measurements during the 5 yr.

Daily variation of pollutants in Bangkok is typical for polluted urban areas, e.g. the Los Angeles smog (Wark et al., 1998). In the early morning rush hours the NMHC, CH_4, and CO concentration peak at around 8:00 a.m. due to traffic. NO peaks at around 7:00 a.m. when O_3 is minimum. NO_2 peaks at around 9:00 a.m., which reflects the time taken for conversion of NO to NO_2 involving HC, and transport of NO_x from upwind locations. NO concentration drops fast after sunrise to its minimum as O_3 increases reaching its highest level

Table 4
Comparison of monthly mean meteorological data with those averaged for episode days (1 h ⩾ 100 ppbv) for the period 1996–2000[a]

Month	Wind speed ($m\,s^{-1}$)	Temperature (°C)	Relative humidity (%)	Cloud cover (tenth)	Solar radiation ($MJ\,m^{-2}$)	Hour of sunshine (h)	Rainfall (mm)
January	1.1 (0.7)	27.8 (27.8)	67.4 (64.2)	5.0 (4.4)	16.3 (17.3)	7.3 (7.9)	0.5 (0)
February	1.3 (0.9)	28.5 (29.2)	69.3 (66.2)	5.1 (4.3)	17.8 (18.8)	7.8 (8.5)	1.3 (0.3)
March	1.6 (1.5)	30.1 (29.8)	70.2 (63.6)	5.5 (5.3)	22.1 (22.0)	8.2 (8.2)	0.8 (1.3)
April	1.3 (0.9)	30.3 (30.0)	73.1 (71.7)	6.5 (6.3)	20.8 (20.9)	7.5 (7.5)	4.8 (4.1)
May	1.1 (1.1)	30.1 (30.6)	73.8 (71.1)	7.2 (6.6)	20.4 (20.2)	7.3 (7.5)	8.9 (6.0)
June	1.2 (1.2)	29.8 (29.7)	72.8 (70.6)	7.5 (6.9)	19.4 (21.7)	5.5 (5.7)	5.1 (3.2)
July	1.3 (1.0)	29.3 (29.8)	73.8 (74.8)	8.0 (7.8)	17.9 (18.9)	4.5 (5.7)	5.3 (12.8)
August	1.2 (1.4)	29.1 (29.6)	74.2 (72.4)	8.0 (7.3)	17.5 (14.7)	4.7 (5.2)	7.0 (14.4)
September	0.9 (0.9)	28.4 (28.5)	78.9 (79.0)	8.3 (8.2)	15.6 (13.6)	4.1 (2.5)	11.5 (13.2)
October	0.8 (0.6)	28.6 (29.2)	77.6 (75.3)	7.5 (7.1)	15.4 (17.4)	5.3 (6.3)	8.9 (5.0)
November	0.9 (0.9)	28.2 (28.4)	69.6 (69.7)	5.9 (4.7)	15.8 (16.6)	6.2 (7.1)	1.9 (2.3)
December	0.9 (0.8)	27.0 (27.7)	62.8 (64.4)	5.0 (5.6)	15.9 (16.4)	7.2 (6.6)	0.1 (0.3)

[a] Values in parenthesis are the episode day averages.


January
August
No.6
No.7
No.8
No.10
NO
NO2
O3
CO*20
CH4*20
NMHC*20

around 13:00–15:00. Besides being consumed in the photochemical reactions, the reduction of pollutant concentrations during the afternoon hours when O_3 is max, should also be caused by the diurnal variation of ventilation in the city as both wind speed and mixing height increase to a maximum in the afternoon.

When comparing the peak concentrations of O_3 precursors between dry and wet season at a station as well as between the four selected stations it is worth mentioning that the stations selected are located on the NE–SW direction across the city center (Fig. 1). Thus station 10 would be mostly downwind of the city center in dry season, when the wind is mostly NE, and upwind during August when the wind is mostly SW. It is seen that significantly higher morning peaks of NO (57 ppbv), NO_2 (36 ppbv), CO (2.9 ppmv) and NMHC (2.5 ppmC) are present as compared to the August corresponding values of 39 ppbv, 18 ppbv, 1.7 ppmv and 1.5 ppmC, respectively. The opposite picture should be observed for stations 6 and 7. The differences in precursor pollutant peaks between January and August at both stations are not significant, which may be due to the counter act of the transport of pollutants from the city center. Station 8 located at the city center should not be affected much by the seasonal change of wind directions. It is noted that the NO peaks at station 8 are the highest of all 4 considered stations that is the reason for the lowest O_3 at this station as compared to other stations.

3.4. Surface meteorological conditions and O_3 episodes

Analysis of monthly windrose for 10 yr (1991–2000) shows high percentage of calm conditions, ranging from 30% in March to 61% in October. The wind direction reflects the typical monsoon circulation. Wind in wet season is mostly from the Westerly to Southerly, bringing relatively clean ocean air masses from the Gulf of Thailand and Andaman Sea to Bangkok. During November–January, when Northerly and NE wind predominate, the higher polluted air masses come cross the Asian continent to Bangkok bring O_3 and O_3 precursors to the study area. In addition, in the dry season there is competing effect between sea breeze (southerly) and NE monsoon resulting in the low wind to calm wind conditions over the city hence reducing the dispersion. It worth mentioning that the NE wind during the dry season is associated with extension of high pressure ridges from southern China to South-East Asia which is expected to reduce the mixing height and limit the dilution of pollutants, especially during the cooler months. Ventilation is further limited during the stationary phase of the ridge when wind is light. Besides, the dry weather and clear sky associated with the ridges also favor O_3 formation. On the contrary, during the wet season air is normally unstable due to the association with the intertropical convergence zone (ITCZ), which favors vertical mixing and hence dilution of pollutants.

As shown in Table 3 ozone episodes in BMR are present throughout the year. To gain insight into the relationship between ozone episodes and the meteorological conditions, surface meteorological data were analyzed separately for the episode days (based on observations from 8 ambient stations) as compared to the respective monthly mean values (Table 4). For episode days, relative humidity and cloud cover are lower, and hours of sunshine are generally higher in comparison with the average conditions. No significant difference in wind speed, temperature, and solar radiation was found between episode and normal days. Intense solar radiation, high temperature and light wind favoring the formation of high levels of O_3 are common for BMR for all the year, hence O_3 episodes can be observed at any season. Low wind speed ($<2.0\,m\,s^{-1}$) is observed throughout the year, implying that episodes are most probably produced by emissions from local sources.

3.5. O_3 isopleth diagram and seasonal variation of NO_x/NMHC ratio

NO_x (NO and NO_2) and NMHC are the essential precursors for the photochemical O_3 production. The optimum NO_x/NMHC ratio for O_3 production available in literature varies within the range from 0.05 to 0.1. The ratios may be changed depending on the compositions of NMHC (Dodge, 1984). For example, Lin et al. (1988) obtained a ratio of about 0.05 based on box model study and Saito et al. (2002) reported a ratio of about 0.1 based on selected observational data.

Observational data study is, in general, different from the numerical simulation. Besides chemical reactions that control the O_3 concentration, the observational O_3 isopleth diagrams include all processes such as transport, deposition and mixing (Saito et al., 2002). To generate O_3 isopleth diagram and estimate seasonal variations in NO_x/NMHC ratios for BMR, the maximum values of NO_x and NMHC concentrations in the early morning (4:00–6:00, before sunrise) observed from 7 ambient stations during 1996–2000 were used, and the amount of increase O_3 (ΔO_3) was determined as the

Fig. 4. Average concentrations of ozone and precursors at Nos. 6, 7, 8 and 10 stations. Vertical bars represent two standard errors of mean values. The values for NO, NO_2, and O_3 are in ppbv; the values of CO, CH_4, and NMHC in ppmv (ppmC for NMHC) multiplied by 20.

difference between the maximum value during the day and the minimum value in the early morning (4:00–6:00). Thompson et al. (2001) reported that El Niño period from March 1997 to April 1998 modified wind fields and precipitation and hence led to an outbreak of forest fire in the region. During this period it was observed that ozone precursors of NMHC and CO from biomass burning were transported to Southeast Asian countries. To reflect the typical local O_3 formation conditions the El Niño period was excluded. Fig. 5 shows the ΔO_3 isopleth diagram ($\Delta O_3 \geqslant 60$ ppb) and Fig. 6 shows the seasonal variations of NO_x/NMHC in the period without El Niño.

Generally, the lower NO_x and NMHC concentrations correspond to the lower ΔO_3 values, whereas the higher NO_x and NMHC concentrations correspond to the higher ΔO_3 values. NO_x/NMHC ratios corresponding to higher ΔO_3 values are in the range of 0.04–0.15, and the optimum ratio is about 0.07 (Fig. 5). The estimated ratios are in a wide range (Fig. 6) with the average of around 0.03, 0.05, and 0.07 for rainy, winter, and summer season, respectively. The O_3 production condition related to precursors is likely more favorable in the local summer and followed by winter. This is consistent with O_3 episode statistical results shown in Table 3 with the highest frequency of photochemical episodes presented in the local summer of February–April, lower in the winter of November–January, and lowest in the rainy season of June and September.

Pitts and Pitts (1993) and Jenkin and Clemitshaw (2000) reported that the following reactions of nitrogen oxides occur predominantly in the atmosphere during nighttime.

$$NO_2 + O_3 \rightarrow NO_3 + O_2, \quad (1)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M, \quad (2)$$

$$N_2O_5 + H_2O \xrightarrow{\text{surface particles}} 2HNO_3. \quad (3)$$

M is any energy-accepting third body, such as N_2 or O_2. N_2O_5 undergoes hydrolysis to form HNO_3. More water vapor content is present in rainy season, hence more NO_2 is consumed than other seasons. For other seasons, the difference of NO_x/NMHC ratio may be due to emission sources. NMHC emission is a function of temperature, and the seasonal contributions of the major NMHC emission sources are influenced by ambient temperature (Saito et al., 2002; Na and Kim, 2001). For the tropical city of Bangkok, temperature does not change much during a year (Table 4), hence temperature change may not play a significant role in the seasonal variation of NO_x/NMHC.

The difference in ratios between winter and summer may be due to local sources in BMR rather than long-range transportation of ozone precursors because of low wind speed ($<1.0\,m\,s^{-1}$) in early morning. Winter season is in rice straw burning period in Thailand. There are numerous rice fields in Pathumthani province (Fig. 1), which is upwind (north) of Bangkok during winter. Thus substantial NMHC may be transported to the city, hence reducing the ratio of NO_x/NMHC in this

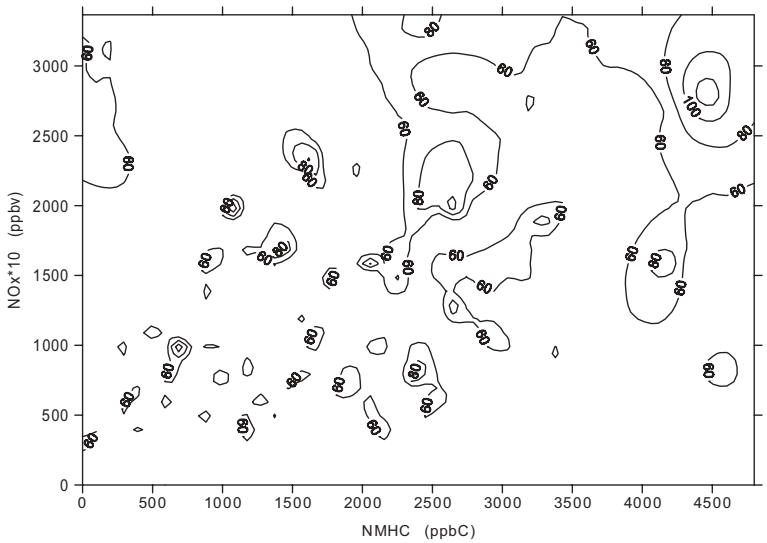


Fig. 5. ΔO_3 isopleth diagram shown only for $\Delta O_3 \geqslant 60$ ppbv based on observational data from 7 general ambient stations (Nos. 4–10) for the period 1996–2000 excluding 1997. The maximum concentrations of NO_x and NMHC in the early morning (4:00–6:00) are used, and O_3 increase (ΔO_3) is determined as the difference between the maximum value during the day and the minimum value in the early morning (4:00–6:00).

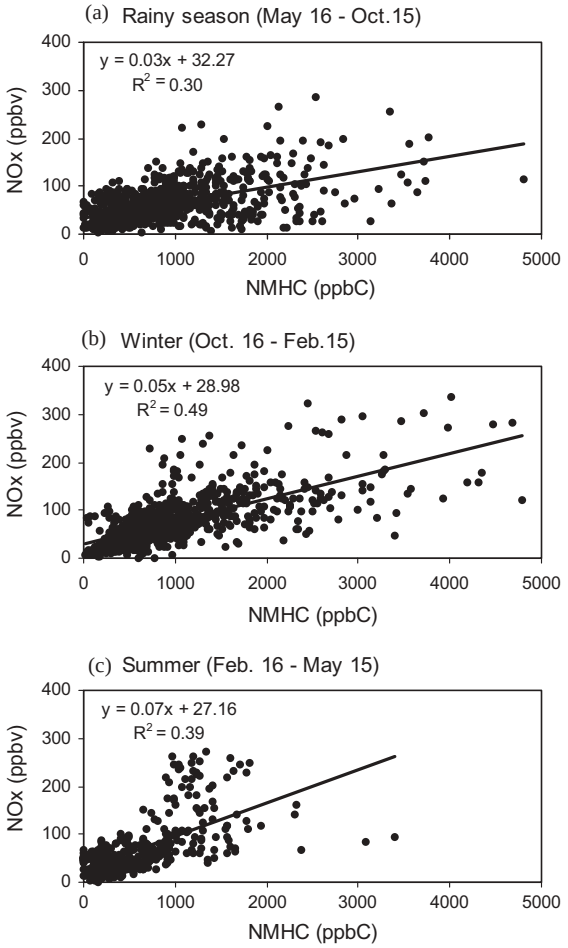


Fig. 6. The seasonal variations in NO_x/NMHC ratios: (a) rainy season, (b) winter, and (c) summer.

period. Details on the contribution of this agricultural burning source is not yet, however, available.

4. Conclusions

Ozone formation and accumulation in Bangkok reflect the interaction of local emission and photochemistry as well as the urban and regional transport of the pollutant and its precursors to the study area. Photochemical smog potential in Bangkok is high due to the high local emission of O_3 precursors and the favorable meteorological conditions, i.e. high temperature and high solar radiation and low wind speed. Spatial distribution of O_3 with the lower levels at the city center, especially at curbside stations, reflects the titration effect of NO emitted from mobile sources. This titration effect also lowers the monthly average of hourly O_3 observed in Bangkok as compared to the remote sites. Local emission and photochemistry in Bangkok are responsible for the high temporal variations of O_3 in the city resulting in frequent O_3 episodes. The Asian monsoon with associated typical local meteorological conditions and the regional transport is the main factor causing the seasonal variations of O_3.

The optimum NO_x/NMHC ratio for O_3 production in BMR, obtained from O_3 isopleth diagram, is about 0.07, which is the value observed in summer. Photochemical potentials estimated from seasonal variations of NO_x/NMHC ratios are consistent with observed seasonal variations of O_3 pollution, showing more effective O_3 production in summer, followed by winter, and the lowest in rainy season.

Interactions of local emission, local and regional meteorological conditions in the formation and accumulation of O_3 are important for development of efficient and cost-effective O_3 pollution management strategies. Further studies are necessary to better understand the synoptic meteorological transport processes especially for high ozone days.

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