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Analyses of the Ozone Weekend Effect in Tokyo, Japan: Regime of Oxidant (O_3 + NO_2) Production

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ABSTRACT

The ozone weekend effect (OWE) in Tokyo, the capital of Japan, was analyzed from April 2005 to March 2008 with respect to the photochemical ozone production, focusing on the ozone production regime. For most periods, the OWE was confirmed in the wintertime as well as in the summertime. The comparison of O_x ($[O_x] = [O_3] + [NO_2] - 0.1[NO_x]$) concentrations between weekdays and weekends suggests that there are some periods when the photochemical ozone production on the weekends could be larger than on the weekdays (defined as the POP group). We compared NO_x (the sum of NO and NO_2) and O_x concentrations on the weekends with those on the weekdays for several distinct ranges of the non-methane hydrocarbons (NMHCs) concentrations, and NO_x and O_x concentrations on the weekends are significantly lower and higher than those on the weekdays in the POP group. Therefore, the ozone production regime would be NMHC-limited in the POP group. The ozone production regime in the summertime in Tokyo could be in the boundary area between NMHC- and NO_x-limited in terms of the NMHCs/NO_x ratios. The NMHCs/NO_x ratios in the NMHC-limited regime are smaller than those in the NO_x-limited regime in general. However, the NMHCs/NO_x ratios in the POP group were not smaller than those in the non-POP group.

Keywords: Ozone weekend effect; Ozone production regime; Nitrogen oxides; Non-methane hydrocarbons.

INTRODUCTION

Tropospheric ozone, a main component of photochemical smog, is a crucial air pollutant in the atmosphere. Ozone causes health problems such as respiratory diseases (Ho *et al*., 2007; Karakatsani *et al*., 2010; Neidell and Kinney, 2010). In addition, ozone has harmful effects on vegetation (Heath *et al*., 2009; Watanabe *et al*., 2010). Ozone in the troposphere is generated by the reactions involving nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) as represented by non-methane hydrocarbons (NMHCs) in the presence of solar ultraviolet. In particular, O_3 is formed via the photolysis of NO_2:

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O(^3P), \quad (1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M, \quad (2)$$

where M represents a third-body molecule such as N_2 and O_2 in the troposphere. The inverse of these two reactions regenerates NO_2 and O_2, as described by the following reaction:

$$NO + O_3 \rightarrow NO_2 + O_2. \quad (3)$$

Reactions (1)–(3) form the photostationary state of NO_x in the daytime (Hauglustaine *et al*., 1996; Carpenter *et al*., 1998; Matsumoto *et al*., 2006). The rate of the photochemical ozone production is determined substantially by the reaction of NO with peroxy radicals (RO_2 and HO_2):

$$RO_2 + NO \rightarrow RO + NO_2, \quad (4)$$

$$RO + O_2 \rightarrow R'COR'' + HO_2, \quad (5)$$

$$HO_2 + NO \rightarrow OH + NO_2, \quad (6)$$

where R, R' and R'' indicate organic groups. Peroxy radicals are generated by the reaction of OH with NMHCs and CO:

$$OH + NMHCs \rightarrow R + H_2O, \quad (7)$$

$$R + O_2 + M \rightarrow RO_2 + M, \quad (8)$$

$$OH + CO \rightarrow H + CO_2, \quad (9)$$

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$$H + O_2 + M \rightarrow HO_2 + M. \quad (10)$$

Reactions (4)–(10) form a chain reaction centered on RO_x (= $OH + HO_2 + RO_2$) radicals to generate tropospheric ozone. The main primary source of RO_x radicals is the reaction of water vapor with $O(^1D)$ atoms which are produced by photodissociation of O_3. Two OH radicals per an ozone molecule are generated via the following reactions:

$$O_3 + h\nu\ (\lambda < 329\ \text{nm}) \rightarrow O_2 + O(^1D), \quad (11)$$

$$O(^1D) + H_2O \rightarrow 2OH. \quad (12)$$

In summary, NO_x and NMHCs are precursors of O_3 and the appropriate reductions of both are important to control ozone concentrations in the troposphere. However, ozone concentrations have been recently increasing, despite a decrease in the concentrations of NO_x and NMHCs in some regions (e.g. Chou *et al*., 2006). In Japan, for example, the recent ozone increase is confirmed by continuous measurements at the numerous air monitoring stations in Tokyo (Tokyo Metropolitan Government, 2005).

The ozone "weekend effect" (e.g. Bronnimann and Neu, 1997; Atkinson-Palombo *et al*., 2006; Sadanaga *et al*., 2008; Stephens *et al*., 2008; Tonse *et al*., 2008) appears to be analogous to the recent increase in ozone concentrations. Ozone concentrations during the weekends are higher than those on the weekdays despite the presence of lower concentrations of NO_x and NMHCs. CARB (California Air Resource Board, 2001) reports several hypotheses for the cause of the ozone weekend effect (OWE). Two of these hypotheses, "ozone quenching hypothesis" and "NO_x reduction hypothesis", appear to be important in verifying the relationship between ozone and its precursors (NMHCs and NO_x) for the OWE. The "ozone quenching hypothesis" is based on the titration of ozone by NO (reaction (3)), which is emitted more abundantly in the urban area on weekdays than on weekends. The "NO_x reduction hypothesis" is related to the chain reaction that produces ozone as described by reactions (4)–(10). NMHCs play a role of the propagator in the chain reaction. The role of NO_x in the ozone production is more complex. NO_x is the direct ozone precursor as described in reactions (1) and (2). On the other hand, NO_x is also an important terminator of the ozone-producing chain reaction because of the following reaction:

$$OH + NO_2 + M \rightarrow HNO_3 + M. \quad (13)$$

In the case of low NO_x mixing ratios, ozone production rates rise when NO_x concentrations increase, that is so-called "NO_x-limited" regime. In the NO_x-limited regime, reactions (4) and (6) are important, and an increase in NO increases the ozone production rate. In the case of high NO_x mixing ratios, ozone production rates decrease when NO_x concentrations increase, that is so-called "NMHC-limited" regime. Reaction (13) becomes significant in the OH radical reactions due to competition between reactions (7) and (13) in the NMHC-limited regime. Therefore, the increase in NO_x concentrations decreases the chain length of the ozone-producing chain reaction. An important factor in determining the ozone production regime (i.e., NO_x-limited or NMHC-limited) is the ratio of NMHCs to NO_x. This ratio indicates that the ozone production rate is determined with respect to the balance between reactions (7) and (13). In the case of the low NMHCs/NO_x, reaction (13) is favorable and an increase of NO_x suppresses the ozone production rate, that is, the ozone production regime is NMHC-limited. CARB (2001) reports that the boundary area between NMHC- and NO_x-limited regimes is the NMHCs/NO_x ratio of 8–10 ppbvC/ppbv, where "ppbv" is parts per billion by volume and "ppbvC" is parts per billion by volume on carbon basis.

In Japan, the OWE analyses were conducted in Tokyo and Osaka, the largest cities in Eastern and Western Japan, respectively (Sadanaga *et al*., 2008). Sadanaga *et al*. (2008) confirmed the existence of the OWE in both Tokyo and Osaka. The OWE in Osaka was found to be due to the titration of O_3 by NO according to the quenching hypothesis. On the other hand, increased photochemical production of ozone due to the NO_x reduction hypothesis could not be neglected as a cause of the OWE in Tokyo. This paper reports analyses of the OWE in Tokyo in terms of photochemical ozone production, focusing on the ozone production regime. In addition, the OWE in wintertime is also analyzed in this article although the report by Sadanaga *et al*. (2008) stated the OWE in only summertime.

SITE DESCRIPTION AND DATA ANALYSES

Fig. 1 shows the location of selected air quality stations in the Tokyo Metropolitan area. Tokyo is the capital of Japan, and is the largest metropolitan area in Japan, with a population in 2010 of approximately 13,000,000. Central Tokyo, the "special ward", is the most crowded area in Japan (the east area in Tokyo, see Fig. 1). As of 2010, central Tokyo's population was about 8,800,000, with an average population density of about 14,100 people/km^2.

The OWE was analyzed using data measured in the monitoring stations for air pollution administrated by the government. We selected 23 air monitoring stations in Tokyo (Fig. 1). The stations in the "special ward" in Tokyo were numbered 1–13 (see Fig. 1). We classified stations 1–13 (in special ward) into "urban" and the remaining stations into "suburbs". We used hourly ozone, NO, NO_2, NO_x and NMHCs data from April 2005 to March 2008. VOC concentrations would be more appropriate to analyze the OWE, however, only the NMHCs data were available. Measurement principles of O_3, NO_x, and NMHCs are based on UV absorption, NO-O_3 chemiluminescence, and flame ionization detector with GC-backflush system to separate CH_4 off, respectively. NMHCs in this article mean the total NMHCs. The data were divided into "weekday" and "weekend," where "weekend" was defined as Saturday, Sunday and national holidays. Averaged diurnal patterns, as depicted in Fig. 2, were calculated for periods A (from January to March), B (from April to June), C (from July to September) and D (from October to December). For example, in this article "2006B", is defined as the period from April

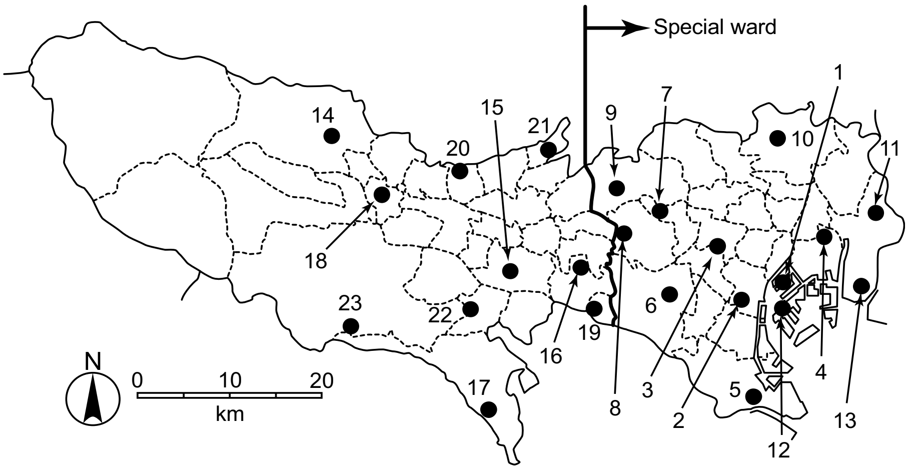

Fig. 1. Locations of selected air monitoring stations in Tokyo. Dashed lines indicate the boundary lines of municipalities. Numbers represent the station code numbers used in this paper. The "special ward" in Tokyo is the east of the bold line.

to June in 2006. The peak value during the day was used for ozone and O_x concentrations (see the next section for a definition of O_x).

RESULTS AND DISCUSSION

Existence or Nonexistence of the OWE

Fig. 2 shows an example of the diurnal patterns of ozone, NO_x and NMHCs on weekdays and weekends. For ozone precursors (i.e., NO_x and NMHCs), their concentrations at the time of the peak value of NO were used, which is the primary product of vehicle exhaust and usually peaks between 06:00 and 09:00 in the morning. On the other hand, the ozone concentrations have a peak value between 13:00 and 16:00. These are typical diurnal variations in the urban atmosphere in Japan.

Table 1 shows weekday-weekend differences of ozone, NO_x and NMHCs in summertime (see the supplementary data for each site). In this paper, "summertime" means "from April to September". The statistical significance was tested using the non-parametric Wilcoxon-Mann-Whitney test. In this article, "significantly" means "with statistical significance". NO_x concentrations on the weekends were significantly lower than those on the weekdays for all periods. On the other hand, there are some periods when NMHCs concentrations on the weekends were significantly higher than those on the weekdays. Concentrations of O_3 on the weekends were found to be significantly larger than those on weekdays, except in the total and suburbs in 2006B, in the suburbs in 2007C. This result clearly shows that the OWE was present in most cases.

Table 1 also lists weekday-weekend differences of the "oxidant" (O_x), which indicates the sum of O_3 and NO_2 concentrations (e.g., White, 1997; Itano *et al*., 2007; Sadanaga *et al*., 2008). It should be noted that NO_2 in O_x should represent the concentration of NO_2 generated secondarily by the oxidation of NO in the atmosphere. NO_2 emitted primarily from combustion sources such as vehicle exhaust should therefore be excluded in order to evaluate O_x correctly. We defined 10% of NO_x as the primarily emitted NO_2, which

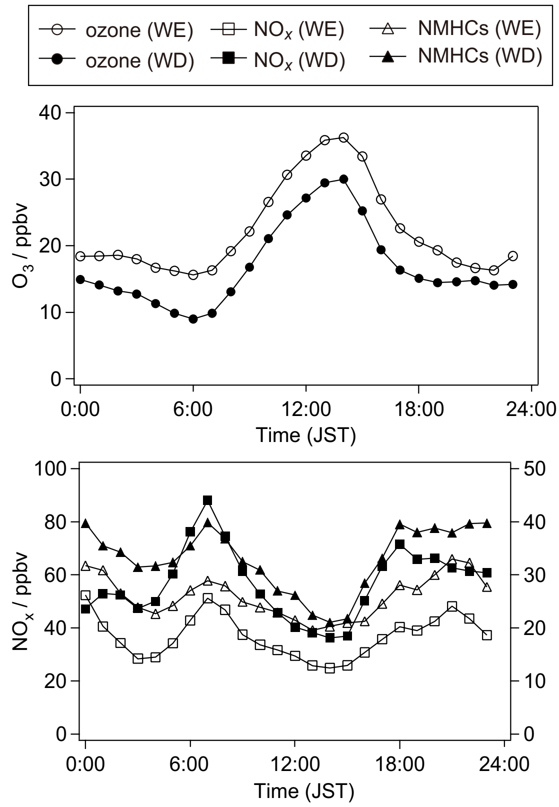

Fig. 2. An example of diurnal variations of ozone, NO_x and NMHCs on weekdays (WD) and weekends (WE) (Station No. 12 in 2006 (period D)).

is based on our previous report (Sadanaga *et al*., 2008). In summary, we defined O_x by the following equation:

$$[O_x] = [O_3] + [NO_2] - 0.1[NO_x]. \tag{14}$$

As described in our previous report (Sadanaga *et al*., 2008), O_x is an indicator to evaluate the "ozone quenching hypothesis". The O_x concentration is conserved in the titration of ozone by NO (reaction (3)). Therefore, O_x on weekend is

Table 1. Weekday-weekend differences of ozone, NO_x, NMHCs and O_x in summertime.

	Ozone [ppbv]			NO_x [ppbv]			NMHCs [0.01ppmvC]			O_x [ppbv]		
	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]
2005B Urban[b]	47.06	58.86	11.80[e]	47.52	35.40	–12.13[e]	24.29	25.99	1.70[c]	70.57	75.82	5.25[e]
2005B Suburbs[b]	58.14	69.96	11.82[e]	36.52	27.24	–9.28[e]	26.21	26.17	–0.04	75.05	81.73	6.68[e]
2005B Total[b]	51.89	63.37	11.48[e]	41.95	31.08	–10.87[e]	25.13	26.07	0.94[d]	72.54	78.21	5.67[e]
2005C Urban[b]	47.07	59.22	12.15[e]	42.72	34.23	–8.49[e]	26.05	27.54	1.49[c]	67.93	76.83	8.90[e]
2005C Suburbs[b]	57.00	64.99	7.99[e]	30.19	24.50	–5.69[e]	26.40	27.79	1.39[c]	72.01	77.62	5.61[e]
2005C Total[b]	51.41	61.74	10.33[e]	37.26	29.99	–7.27[e]	26.20	27.65	1.45[e]	69.72	76.74	7.02[e]
2006B Urban[b]	48.05	50.60	2.55[d]	46.01	27.81	–18.20[e]	27.20	20.79	–6.41[e]	73.45	66.23	–7.22[e]
2006B Suburbs[b]	55.24	54.50	–0.74	32.08	23.50	–8.58[e]	26.24	24.65	–1.59[d]	73.82	65.95	–7.87[e]
2006B Total[b]	51.17	52.08	0.92	40.02	26.36	–13.66[e]	26.78	22.65	–4.13[e]	73.61	66.20	–7.41[e]
2006C Urban[b]	44.00	54.26	10.26[e]	42.28	35.50	–6.78[e]	26.06	29.99	3.93[e]	65.72	70.81	5.09[e]
2006C Suburbs[b]	51.50	57.46	5.96[e]	28.85	23.63	–5.22[e]	27.44	29.08	1.64	66.90	69.73	2.83
2006C Total[b]	47.25	56.20	8.95[e]	36.46	30.38	–6.08[e]	26.66	29.59	2.93[e]	66.23	70.99	4.76[e]
2007B Urban[b]	47.43	59.29	11.86[e]	43.47	28.13	–15.34[e]	24.12	21.39	–2.73	68.11	74.29	6.18[e]
2007B Suburbs[b]	55.23	63.26	8.03[e]	29.81	21.84	–7.97[e]	19.67	18.60	–1.07	69.15	71.70	2.55[e]
2007B Total[b]	50.81	61.48	10.67[e]	37.51	25.39	–12.12[e]	22.19	20.18	–2.01	68.56	73.80	5.24[e]
2007C Urban[b]	42.09	47.75	5.66[e]	41.68	24.83	–16.85[e]	26.44	21.16	–5.28[e]	62.94	59.54	–3.40[e]
2007C Suburbs[b]	50.02	50.67	0.65	30.06	18.53	–11.53[e]	23.46	20.35	–3.11[e]	65.85	60.85	–5.00[e]
2007C Total[b]	45.47	48.78	3.31[c]	36.69	22.14	–14.55[e]	25.16	20.82	–4.34[e]	63.79	59.67	–4.12[e]

[a] WD, WE and Delta indicate weekday, weekend and weekend minus weekday, respectively. [b] Urban, suburbs and total mean the averaged values of the sites 1–13, 14–23 and 1–23, respectively. B and C mean the periods from April to June and from July to September, respectively. [c] Statistically significant with $P < 0.1$. [d] Statistically significant with $P < 0.05$. [e] Statistically significant with $P < 0.01$.

not necessarily higher than that on weekday if the "ozone quenching hypothesis" is a main cause of the OWE.

As listed in Table 1, O_x concentrations on the weekends were found to be significantly greater than those on weekdays in 2005B, 2005C, 2006C and 2007B. In this article, the periods 2005B, 2005C, 2006C and 2007B are brought together into a group defined as the "photochemical ozone production" group (POP group). In the daytime, the O_x concentration increases via the reaction of NO with peroxy radicals:

$$RO_2 + NO \rightarrow RO + NO_2. \quad (4)$$

Ozone is produced via the photolysis of NO_2. In the daytime, reaction (4) is the rate-determining step for ozone production, so that this reaction governs the rate of photochemical ozone production (Sadanaga *et al.*, 2005; Kanaya *et al.*, 2008).

The decrease in O_x concentration is mainly due to the reaction of OH with NO_2:

$$OH + NO_2 + M \rightarrow HNO_3 + M. \quad (11)$$

This reaction functions as an inhibitor against the photochemical ozone production. Hence, O_x increase and decrease indicate promotion and inhibition of photochemical ozone production, respectively. In other words, O_x concentrations are an indicator of photochemical ozone production. In the POP group, O_x concentrations on weekend are greater than that on weekday, so that the photochemical ozone production on weekend would be larger than that on weekday.

Table 2 represents weekday-weekend differences of ozone, NO_x, NMHCs and O_x in wintertime (see the supplementary data for each site). In this paper, "wintertime" means "from October to March". Both NO_x and NMHCs concentrations on the weekends were lower than those on the weekdays for all periods. On the other hand, ozone concentrations on the weekends were greater than those on the weekdays for all periods. It is noteworthy that the OWE was confirmed in the wintertime as well as in the summertime. O_x concentrations on the weekends were not significantly higher than those on weekdays. Therefore, OWE in wintertime can be explained by the "ozone quenching hypothesis".

Diagnosis of Photochemical Ozone Production: Relationship between O_x and its Precursors

The relationship between photochemical ozone production and the concentrations of ozone precursors (i.e., NO_x and NMHCs) is non-linear and complex. As described in Introduction, in the NO_x-limited regime, the production rate of ozone rises when NO_x concentrations increase. Conversely, the production rate of ozone decreases when NO_x concentrations increase, in the NMHC-limited regime. Taking this point into account, we discuss the ozone production regimes as follows. We compared NO_x and O_x concentrations on the weekend with those on weekdays for several distinct ranges of the NMHCs concentrations. If NO_x concentrations are significantly lower and O_x concentrations are significantly higher on weekends compared to weekdays, then the ozone production regime could be NMHC-limited. It should be noted that O_x instead of O_3 was used in this analysis because O_x concentrations are more appropriate indicator of photochemical ozone production as described above.

Table 2. Weekday-weekend differences of ozone, NO_x, NMHCs and O_x in wintertime.

	Ozone [ppbv]			NO_x [ppbv]			NMHCs [0.01ppmvC]			O_x [ppbv]		
	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]	WD[a]	WE[a]	Delta[a]
2005D Urban[b]	26.74	33.44	6.70[e]	86.49	63.43	–23.06[e]	36.06	35.00	–1.06	50.50	52.12	1.67
2005D Suburbs[b]	32.57	37.80	5.23[e]	73.46	49.11	–24.35[e]	32.32	29.08	–3.24[e]	48.77	50.54	1.77
2005D Total[b]	29.31	35.34	6.03[e]	80.83	57.24	–23.59[e]	34.43	32.44	–1.99[d]	49.75	51.44	1.69
2006A Urban[b]	29.67	36.00	6.33[e]	75.95	50.84	–25.11[e]	30.21	25.70	–4.51	53.49	51.59	–1.90
2006A Suburbs[b]	36.20	40.19	3.99[e]	63.60	42.31	–21.29[e]	28.49	24.82	–3.67[c]	54.16	51.96	–2.20[c]
2006A Total[b]	32.36	37.82	5.46[e]	70.63	47.15	–23.48[e]	29.44	25.30	–4.14	53.52	51.75	–1.77[c]
2006D Urban[b]	25.34	33.62	8.28[e]	74.51	43.87	–30.64[e]	33.99	26.73	–7.26[e]	50.25	50.36	0.11
2006D Suburbs[b]	31.37	35.99	4.62[e]	59.37	35.85	–23.52[e]	28.76	24.67	–4.09[e]	49.65	49.27	–0.38
2006D Total[b]	27.95	34.65	6.70[e]	67.93	40.39	–27.54[e]	31.73	25.83	–5.90[e]	49.99	49.89	–0.10[c]
2007A Urban[b]	31.91	34.42	2.51[e]	67.88	43.31	–24.54[e]	26.91	23.03	–3.88[e]	55.93	52.05	–3.87[e]
2007A Suburbs[b]	37.86	39.06	1.20	66.76	38.09	–28.67[e]	25.63	20.05	–5.58[e]	54.84	52.14	–2.70[e]
2007A Total[b]	34.48	36.39	1.91[e]	67.39	41.04	–26.35[e]	26.35	21.74	–4.61[e]	55.45	52.08	–3.37[e]
2007D Urban[b]	24.98	32.48	7.50[e]	78.86	49.79	–29.07[e]	35.59	28.52	–7.07[e]	50.14	48.85	–1.29[d]
2007D Suburbs[b]	29.66	35.14	5.48[e]	65.89	40.35	–25.54[e]	28.65	22.72	–5.93[e]	49.22	47.29	–1.93[d]
2007D Total[b]	27.01	33.64	6.63[e]	73.25	45.70	–27.55[e]	32.59	26.02	–6.57[e]	49.75	48.17	–1.58[e]
2008A Urban[b]	32.04	40.60	8.56[e]	73.96	38.43	–35.53[e]	28.36	19.85	–8.51[e]	53.02	52.29	–0.72[e]
2008A Suburbs[b]	38.04	43.98	5.94[e]	63.16	31.17	–31.99[e]	24.89	16.49	–8.40[e]	53.64	53.06	–0.58[d]
2008A Total[b]	34.64	42.06	7.42[e]	69.38	35.32	–34.06[e]	26.84	18.40	–8.44[e]	53.28	52.62	–0.66[e]

[a] WD, WE and Delta indicate weekday, weekend and weekend minus weekday, respectively. [b] Urban, suburbs and total mean the averaged values of the sites 1–13, 14–23 and 1–23, respectively. A and D mean the periods from January to March and from October to December, respectively. [c] Statistically significant with $P < 0.1$. [d] Statistically significant with $P < 0.05$. [e] Statistically significant with $P < 0.01$.

Table 3 shows the weekday-weekend differences for NO_x and O_x for several distinct ranges of NMHCs concentrations in summertime. NO_x and O_x concentrations on the weekends are significantly lower and higher than those on the weekdays, respectively, for the periods of 2005B, 2005C, 2006C and 2007B, which are exactly the POP group. This result would be valid considering the following three points. First, higher O_x concentrations on the weekend than those on the weekdays (i.e. the POP group) mean that the OWE cannot be explained only by the titration of O_3 by NO. Second, the O_x increase is due to reactions (4) and (6) and reflects the photochemical ozone production. Third, NO_x reduction causes the rise of the photochemical ozone production in the NMHC-limited regime. In summary, the POP group must be in NMHCs-limited regime, so that the "NO_x reduction hypothesis" is one of the factors of the OWE for the POP group. The non-POP group would be in NO_x-limited because the both NO_x and O_x concentrations on the weekends are significantly lower than those on the weekdays for several distinct ranges of NMHCs concentrations. It should be noted that the regime for O_3 might be different from those inferred for O_x here. For example for the non-POP group, O_x concentrations are smaller on weekend than those on weekday but that is not the case for O_3 concentrations. Nonetheless, we focus on the regime for O_x here that should describe the photochemical tendency more correctly.

CARB (2001) reports that the boundary area between NMHC- and NO_x-limited regimes is the NMHCs/NO_x ratio of 8–10 ppbvC/ppbv, which is roughly in agreement with that suggested by Milford *et al.* (1994) (10–20 ppbvC/ppbv). Hence such ozone production regimes are discussed in terms of NMHCs/NO_x ratios. Table 3 also lists the weekday-weekend differences of NMHCs/NO_x ratios for several distinct ranges of the NMHCs concentrations. The NMHCs/NO_x ratios on the weekend were higher than those on the weekdays in all the cases aside from statistical significance. The NMHCs/NO_x ratios in summertime ranged from 5.10 to 18.81 ppbvC/ppbv, which are roughly in agreement with the boundary area between NMHC- and NO_x-limited regimes reported by Milford *et al.* (1994) and CARB (2001). Therefore, the ozone production regime in the summertime could be in the boundary area between NMHC- and NO_x-limited with respect to the NMHCs/NO_x ratios. In general, the NMHCs/NO_x ratios in the NMHC-limited regime are smaller than those in the NO_x-limited regime. In the summertime, the NMHCs/NO_x ratios ranged from 5.10 to 11.22 ppbvC/ppbv in the POP group. On the other hand, the NMHCs/NO_x ratios in the non-POP group ranged from 6.12 to 18.81 ppbvC/ppbv. The NMHCs/NO_x ratios in the POP group were not significantly smaller than those in the other periods. In order to discuss ozone production rates more specifically, the use of the VOC reactivity, that is, the reactivity of VOCs with OH radicals, is more appropriate than the VOC concentration (Sillman, 1999). In addition, the critical NMHCs/NO_x ratio separating the two regimes can vary with the primary RO_x production rate (P_{ROx}) (Thornton *et al.*, 2002). The variation of the boundary area with P_{ROx}, and the composition of NMHCs might cause the present result in summertime.

Table 4 represents the weekday-weekend differences for NO_x and O_x for several distinct ranges of NMHCs concentrations in wintertime. Both NO_x and O_x concentrations on the weekends are lower than those on the weekdays, that is, the ozone production regime in wintertime is in

Table 3. Weekday-weekend differences of NO_x, O_x and ratios of NMHCs to NO_x for the same intervals of NMHCs concentrations in summertime.

Period[g]	NMHCs [ppmvC]	*S.N.*[f] WD[a]	*S.N.*[f] WE[a]	NO_x [ppbv] WD[a]	NO_x [ppbv] WE[a]	NO_x [ppbv] Delta[a]	O_x [ppbv] WD[a]	O_x [ppbv] WE[a]	O_x [ppbv] Delta[a]	NMHCs/NO_x [ppbvC/ppbv] WD[a]	NMHCs/NO_x [ppbvC/ppbv] WE[a]	NMHCs/NO_x [ppbvC/ppbv] Delta[a]
2005B[b]	0.1–0.2	4	3	28.80	18.20	–10.60[c]	72.83	83.42	10.59	6.77	9.91	3.14[d]
	0.2–0.3	13	15	48.99	34.56	–14.43[e]	71.35	77.25	5.90[e]	5.46	7.81	2.36[e]
	0.3–0.4	6	5	42.84	32.93	–9.91[d]	75.30	79.46	4.17[d]	7.76	10.27	2.51[d]
2005C[b]	0.1–0.2	2	2	20.23	16.00	–4.23	70.86	75.21	4.35	7.44	10.33	2.89
	0.2–0.3	15	13	40.41	32.36	–8.05[d]	69.26	75.43	6.17[e]	6.46	8.28	1.82[d]
	0.3–0.4	6	8	38.78	30.55	–8.23[d]	71.78	79.33	7.55	9.10	11.22	2.12
2006B[b]	0.1–0.2	3	8	39.14	26.07	–13.07	69.07	63.79	–5.28	6.22	7.12	0.91
	0.2–0.3	15	13	42.12	27.02	–15.10[e]	74.44	67.53	–6.91[e]	6.58	9.77	3.19[e]
	0.3–0.4	5	2	39.33	27.09	–12.24[c]	74.16	67.25	–6.92[c]	8.62	14.13	5.51[c]
2006C[b]	0.1–0.2	3	2	45.46	31.31	–14.15	68.22	71.01	2.78	5.10	8.10	3.00
	0.2–0.3	15	12	35.45	29.85	–5.59[c]	67.64	71.97	4.33[d]	7.89	10.01	2.12[c]
	0.3–0.4	5	8	37.28	32.41	–4.87	63.06	72.51	9.45[d]	9.34	10.55	1.31
2007B[b]	0.1–0.2	7	11	33.07	24.23	–8.84	68.82	73.83	5.01[e]	5.27	7.4	2.15[c]
	0.2–0.3	15	12	41.10	26.94	–14.16[e]	68.74	73.82	5.08[e]	6.35	8.84	2.49[e]
2007C[b]	0.1–0.2	6	12	32.45	23.03	–9.42	64.42	58.93	–5.49[d]	6.12	7.98	1.86
	0.2–0.3	11	9	40.90	22.35	–18.55[e]	63.03	62.03	–1.00	6.45	10.83	4.38[e]
	0.3–0.4	6	2	37.17	18.90	–18.27[c]	66.28	59.85	–6.43	9.41	18.81	9.40[c]

[a] WD, WE and Delta are weekday, weekend and weekend minus weekday, respectively. [b] A and D mean the periods from January to March and from October to December, respectively. [c] Statistically significant with $P < 0.1$. [d] Statistically significant with $P < 0.05$. [e] Statistically significant with $P < 0.01$. [f] Number of samples. [g] The "POP group" periods are underlined in this column.

Table 4. Weekday-weekend differences of NO_x, O_x and ratios of NMHCs to NO_x for the same intervals of NMHCs concentrations in wintertime.

Period	NMHCs [ppmvC]	*S.N.*[f] WD[a]	*S.N.*[f] WE[a]	NO_x [ppbv] WD[a]	NO_x [ppbv] WE[a]	NO_x [ppbv] Delta[a]	O_x [ppbv] WD[a]	O_x [ppbv] WE[a]	O_x [ppbv] Delta[a]	NMHCs/NO_x [ppbvC/ppbv] WD[a]	NMHCs/NO_x [ppbvC/ppbv] WE[a]	NMHCs/NO_x [ppbvC/ppbv] Delta[a]
2005D[b]	0.2–0.3	7	6	69.95	51.63	–18.32[c]	48.66	50.41	1.75	4.02	5.40	1.38
	0.3–0.4	9	10	83.66	65.87	–17.79[e]	50.74	52.37	1.63[c]	4.59	5.47	0.88[e]
	0.4–0.5	5	5	91.07	66.15	–24.91[d]	48.75	51.83	3.08	4.83	6.80	1.97[e]
2006A[b]	0.2–0.3	8	14	72.09	47.28	–24.81[e]	52.90	52.33	–0.58	3.75	5.82	2.07[e]
	0.3–0.4	12	3	73.34	55.08	–18.26[d]	54.12	51.11	–3.01[d]	4.67	5.77	1.10[d]
2006D[b]	0.2–0.3	8	15	63.56	39.54	–24.02[e]	48.99	51.15	2.16[d]	4.27	6.64	2.37[e]
	0.3–0.4	11	4	73.56	49.57	–24.00[e]	51.25	46.75	–4.49[d]	4.88	7.26	2.39[e]
2007A[b]	0.1–0.2	4	9	55.81	36.15	–19.66[c]	53.19	51.21	–1.98[c]	3.54	4.74	1.19
	0.2–0.3	12	13	69.63	44.74	–24.90[e]	55.47	52.64	–2.83[e]	3.71	5.68	1.97[e]
2007D[b]	0.1–0.2	2	6	39.96	35.19	–4.77	47.68	47.12	–0.56	4.66	4.99	0.33
	0.2–0.3	7	10	69.24	46.71	–22.53[e]	49.12	49.47	0.35	3.66	5.53	1.88[e]
	0.3–0.4	8	6	75.92	51.62	–24.31[e]	50.65	48.10	–2.56[c]	4.63	6.36	1.73[e]
2008A[b]	0.1–0.2	5	14	54.57	33.76	–20.81[d]	52.55	53.18	0.63	3.59	5.00	1.41[c]
	0.2–0.3	11	7	68.07	38.93	–29.14[e]	54.00	51.88	–2.12[d]	3.87	5.76	1.89[e]

[a] WD, WE and Delta are weekday, weekend and weekend minus weekday, respectively. [b] A and D mean the periods from January to March and from October to December, respectively. [c] Statistically significant with $P < 0.1$. [d] Statistically significant with $P < 0.05$. [e] Statistically significant with $P < 0.01$. [f] Number of samples.

NO_x-limited for most of the periods. Table 4 also shows the weekday-weekend differences of NMHCs/NO_x ratios for several distinct ranges of the NMHCs concentrations. The NMHCs/NO_x ratios on the weekend were higher than those on the weekdays in all the cases aside from statistical significance. In wintertime, the NMHCs/NO_x ratios ranged from 3.54 to 7.26 ppbvC/ppbv, and the ozone production regime is categorized into NMHC-limited if only the NMHCs/NO_x ratio is considered. In addition, it should be noted that the NMHCs/NO_x ratio in the boundary area between NMHC- and NO_x-limited regimes in wintertime becomes higher than that in summertime. Kanaya *et al.* (2008) predicts the boundary associated with the NMHCs/NO_x of ~20 and ~50 ppbvC/ppbv in summertime and wintertime, respectively. However, the ozone production regimes in wintertime were not NMHC-limited in many cases. Kanaya *et al*. (2008) reported that net O_x production rates in winter in Tokyo based on observations showed NO_x-limited-like behavior, whereas the box model calculation (Kanaya *et al*., 2008) suggested that the ozone production regime was in NMHC-limited. Our result is consistent with the result of Kanaya *et al*. (2008).

CONCLUSIONS

We analyzed the OWE in Tokyo, in terms of photochemical ozone production from April 2005 to March 2008. For most periods, the OWE was confirmed with statistical significance in the wintertime as well as in the summertime. In summertime, O_x concentrations on the weekend were also significantly higher than those on the weekdays in periods 2005B, 2005C, 2006C and 2007B (defined as the POP group). This result suggests the photochemical ozone production on the weekend could be larger than on the weekdays in these periods. In order to diagnose the ozone production regime as a cause of the OWE, we compared NO_x and O_x concentrations on the weekend with those on the weekdays for several distinct ranges of the NMHCs concentrations and we concluded that the ozone production regime would be NMHC-limited and NO_x-limited in the POP group and otherwise, respectively. We also compared the NMHCs/NO_x ratios on the weekend with those on the weekdays for several distinct ranges of the NMHCs concentrations. The NMHCs/NO_x ratios in summertime ranged from 5.10 to 18.81 ppbvC/ppbv, which are roughly in agreement with the boundary area between NMHC- and NO_x-limited regimes reported by Milford *et al*. (1994) and CARB (2001). Therefore, the ozone production regime in the summertime could be in the boundary area between NMHC- and NO_x-limited with respect to the NMHCs/NO_x ratios. On the other hand, the NMHCs/NO_x ratios in the POP group were not significantly smaller than those in the other periods although the NMHCs/NO_x ratios in the NMHC-limited regime are smaller than those in the NO_x-limited regime in general. This might be because the boundary area can vary with $P_{\mathrm{RO_x}}$ and the composition of NMHCs. In wintertime, O_x concentrations on the weekend were not greater than those on the weekdays in most periods, so that the OWE in wintertime can be explained by the titration of ozone by NO. The ozone production regime during the wintertime could be NMHC-limited in terms of the NMHCs/NO_x ratio but is actually NO_x-limited in many periods. It might be insufficient that the ozone production regime in the wintertime is discussed using only the NMHCs/NO_x ratio.

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