SMOG STUDY USING TWIN CHAMBERS FILLED WITH AMBIENT AIR

Kil-Choo Moon, Gwi-Nam Bae, Seung-Bok Lee, Young-Mee Lee, Ji-Eun Choi
Air Resources Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea, kcmoon@kist.re.kr

1. INTRODUCTION

Seoul is one of the most severe smoggy cities in the world. During summer afternoons, the fine particles formed by photochemical reactions could contribute visibility reduction. The formation and growth of secondary ambient aerosols might be affected by primary air pollutants and by meteorological factors. In this work, the photochemical reaction of Seoul ambient air was investigated in indoor smog chambers. Since the quality of ambient air changed with time, the twin chambers were utilized to differentiate the effects of primary particle concentration and light intensity on the formation of ozone and aerosols during the photochemical reaction.

2. EXPERIMENTAL

The experiments of photochemical reaction of ambient air were conducted in two identical smog chambers, as shown in Fig. 1. Each chamber consisted of a housing, a Teflon film bag, 64 blacklights, and injection and sampling ports. The bag, made of 2-mil thick FEP Teflon film, was installed in a temperature-controlled, particle-free cleanroom facility [1]. The volume of the cubic bag was about 5.8 m^3 (1.8×1.8×1.8 m), and the surface-to-volume ratio was 3.3 m^{-1}. The Teflon bag was irradiated by 64 blacklights (Sylvania model F40/350BL, 40W) located both sides of the bag. The light intensity was measured by NO_2 actinometry using a quartz tube. The maximum photolysis rate constant (k_1) for NO_2 was found to be 0.55 min^{-1}, which corresponded to that of the summer noon in Seoul [2].

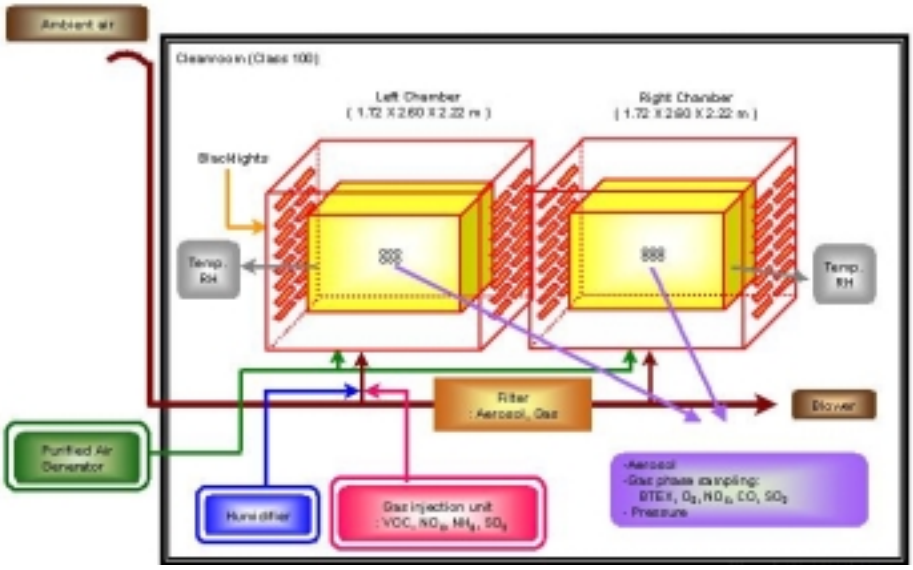


Figure 1. Schematic diagram of the indoor twin smog chambers

During the experiment, O_3, NO-NO_2-NO_x, SO_2, and CO concentrations were measured every minute with continuous analyzers [1]. Toluene concentration was also measured every 25

minutes, by gas chromatography and an FID detection (Agilent model 6890N), using a 0.32 mm × 30 m × 0.25 μm HP-5 column (Agilent). The sample was concentrated with a preconcentrator (Entech model 7100) to detect toluene concentrations of less than 1 ppm.

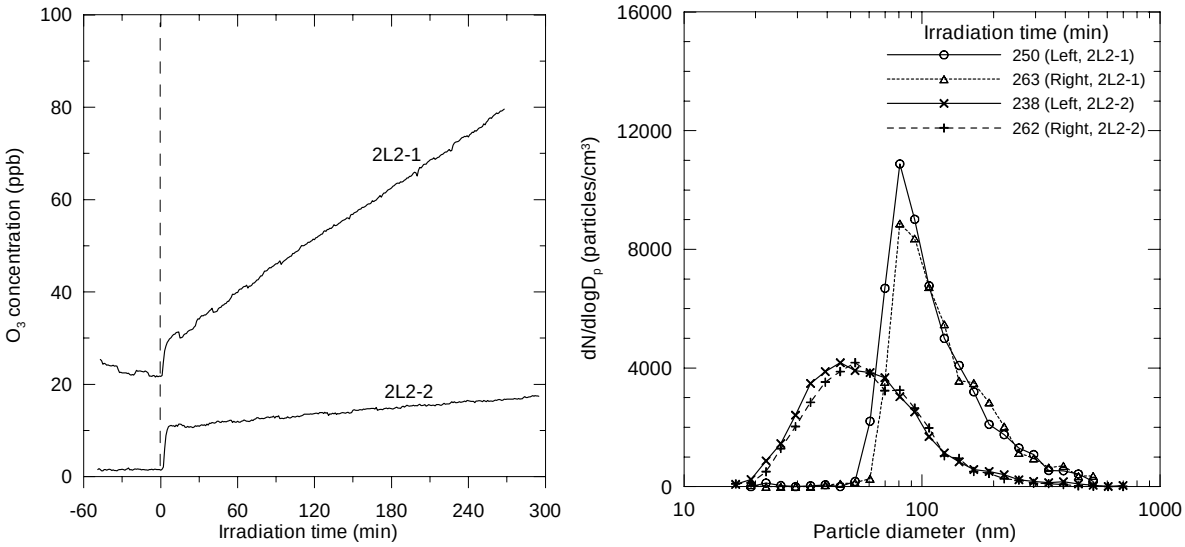
The particle size distribution was measured every 5 minutes using a scanning mobility particle sizer (SMPS, TSI model 3934U) in the size range 16.5~626 nm. The SMPS was composed of an electrostatic classifier (TSI model 3071) and a condensation particle counter (TSI model 3010). The particle mass concentration was calculated from the measured number concentration, assuming that aerosols were unit-density spheres. The air temperature and relative humidity in the bag were also measured using a small sensor and data-logger (Sata Keiryoki model SK-L200Th).

Prior to each experiment, the Teflon bags were flushed with purified air to minimize the effect of bag contamination, and then background reactivity of the bags was confirmed to be low through the photochemical reactions of purified air for several hours [2]. For main experiments, the air in each bag was exchanged with ambient air three times to initialize the bags. Thereafter, the bags were filled with ambient air for about 12~30 minutes. For experiments on the effect of particle reduction, the left chamber was completely filled with unfiltered ambient air. On the other hands, the 33~99-% particles in ambient air were removed using an absolute air filter (Cambridge Filter Korea), and then the filtered air was introduced into the right chamber. For experiments on the effect of light intensity, both chambers were completely filled with unfiltered ambient air. The light intensity of each chamber was changed from 0.14 to 0.55 min^{-1}. The irradiation lasted for about 4 hrs.

The six and twelve sets of chamber experiments were carried out to investigate the effects of initial particle concentration and light intensity, respectively. These experiments were done from September 2003 to June 2004. For each group, initial conditions and experimental results were summarized in Table 1. The performance comparison of two chambers was performed twice at the same light intensity of 0.3 min^{-1}. The variation of ozone concentrations was shown in Fig. 2(a). Considering that only one ozone analyzer was used to measure ozone concentration in two chambers, the ozone concentrations of both chambers seemed to be very similar. Note that the ozone formation rates of two experiments (2L2-1 and 2L2-2) were very different although the light intensities of them were same. The particle size distributions were compared in Fig. 2(b). The formation and condensational growth of aerosols during the photochemical reaction resulted in the change of particle size distribution. The particle size distribution of a left chamber was good agreement with that of a right chamber at a similar irradiation time. From these comparisons, it was concluded that the performance of both chambers was nearly identical.

Parameter	Group	Initial particles (particles/cm^3)	Initial O_3 (ppb)	Initial NO_x (ppb)	Initial toluene (ppb)	Toluene/NO_x (ppbC/ppb)	Δ N for 20-300 nm (particles/cm^3)	O_3 production rate(ppb/min)
Particles	A	<600	2-14	36-128	5.5-10.4	0.5-1.1	>21000	0.073-0.193
	B	1781~3867	16-24	18-36	2.9-6.8	1.0-1.5	3640-6189	0.154-0.195
	C	2639~4982	1-23	18-120	3.6-8.8	0.5-1.8	2682-3446	0.063-0.101
	D	5686~8247	1-2	98-138	9.0-9.8	0.5-0.6	1004-2361	0.055-0.088
Light intensity	A	1434~2397	25-50	6-16	2-19	1.5-9.3	6600	0.18-0.34
	B	1100~1800	5-27	16-34	2-4	0.6-1.1	500-900	0.09-0.15
	C	11000	50	25	6	1.7	13000	0.34
	D	4500~7200	<38	38-63	6-15	0.8-1.7	<900	0.10-0.24

Table 1. Initial conditions and experimental results.



(a) Ozone (b) Particle size distribution

Figure 2. Performance comparison of twin smog chambers.

3. RESULTS AND DISCUSSION

In early stage, the ozone was produced by NO_2 photolysis reaction and the ozone concentration stabilized generally within 4-min irradiation, as shown in Fig. 2(a). Thereafter, the ozone concentration increased almost linearly. So, the ozone production rate was calculated from the concentration gradient between 4 min and final irradiation time. And the particles in the size range 20-300 nm were considered in this work.

3.1 The effect of initial particle number concentration

All experiments were classified into four groups, based on the variation of particle number concentration during the irradiation. Typical trend of particle number concentrations for each group was illustrated in Fig. 3. In case of group A, the aerosol formation was dominant mechanism in early stage of irradiation due to low initial particle concentrations. The aerosol formation decreased with increasing initial particle number concentration. In case of group D, the particle number concentration was nearly unchanged during the irradiation.

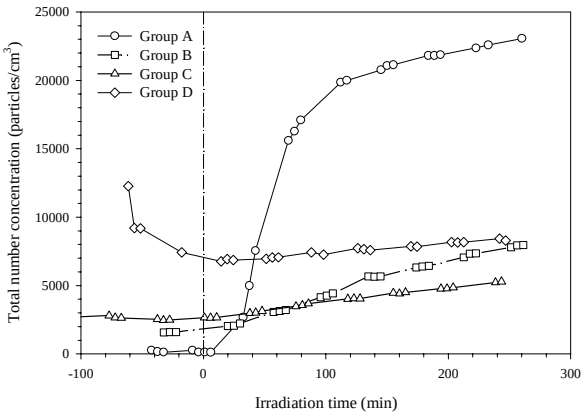
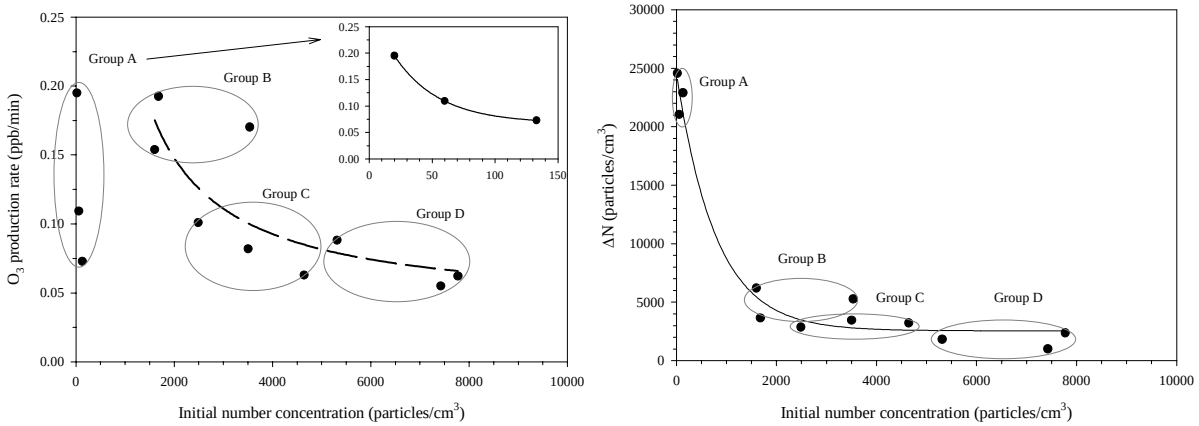


Fig. 3. Typical trends of particle number concentrations.

The effect of initial particle concentration on the formation of ozone and aerosols was shown in Figs. 4(a) and (b). The ozone production rate increased with decreasing initial particle number concentration except for group A. Although the ozone production rate varied in the wide range for group A, it also increased with decreasing initial particle number concentration under 150 particles/cm^3. In this work, the amount of particle formation, Δ N, was defined as a difference between initial particle number concentration (N_i) and final particle number concentration at 250-min irradiation (N_f). The Δ N increased as the initial particle number concentration decreased, which means that the reduction of aerosols might cause adverse health effect due to the increase of ultrafine particles. However, it could contribute to suppress the growth of existing particles. The initial conditions that the initial concentration of NO_x was relatively high, and the concentration ratio of toluene/NO_x was relatively low, were considered to suppress the formation and growth of aerosols for groups C and D.



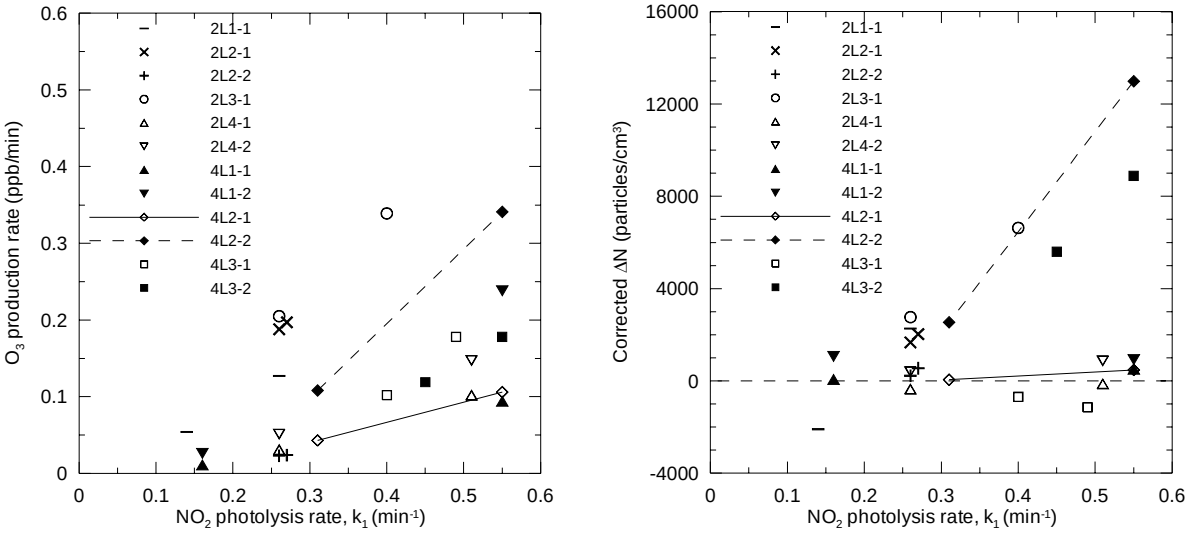
(a) Ozone (b) Aerosols

Figure 4. The effect of initial particle number concentration on the formation of ozone and aerosols.

3.2 The effect of light intensity

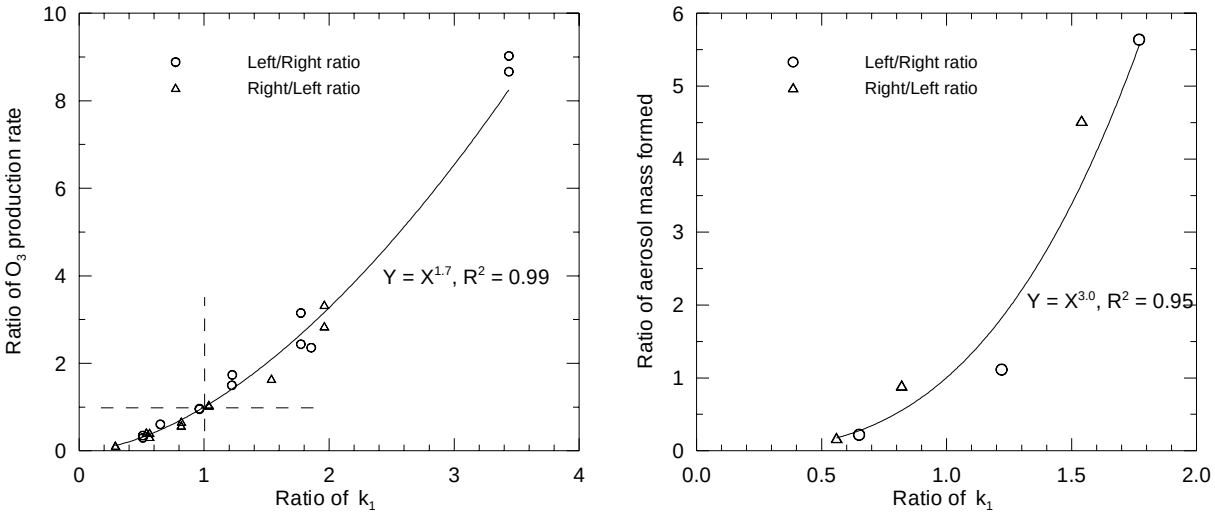
The ozone production rates for all chambers with NO_2 photolysis rate, k_1, were represented in Fig. 5(a). Although the ozone production rate scattered greatly at the similar k_1, it seemed to increase as the k_1 increased. The ozone production rate of the chamber with higher irradiation was greater than that of the chamber with lower irradiation for the same experiment with same initial air quality. The amount of aerosol formation increased as the light intensity increased only when the aerosol formation was clearly observed, as shown in Fig. 5(b). The values less than zero in Fig. 5(b) were caused by the uncertainty of particle wall loss rates. From Figs. 5(a) and (b), it was found that the ozone production rates and the aerosol formation depended highly on the air quality although the light intensity was the same.

To differentiate the effect of light intensity on the formation of ozone and aerosols, experimental results of twin chambers were compared. The ratios of ozone production rates between twin chambers for the same experiment were illustrated in terms of ratio of light intensities, as shown in Fig. 6(a). The relation between two ratios was well represented as a parabolic curve with the power of about 1.7. From this relationship, it was supposed that the double increase of light intensity resulted in about triple increase of ozone production rate when the ambient air quality was favorable for ozone formation. The relationship can be utilized in prediction of ozone concentration formed by photochemical smog.



(a) Ozone (b) Aerosols

Figure 5. The effect of light intensity on the formation of ozone and aerosols.



(a) Ozone (b) Aerosols

Figure 6. The correlation between ratio of light intensity and ratio of ozone production rate or ratio of aerosol mass formed.

The ratios of aerosol mass formed during the irradiation between twin chambers for the same experiment were shown in terms of ratio of light intensities, as shown in Fig. 6(b). The relation between two ratios was well described as a parabolic curve with the power of about 3.0. From this relationship, it was supposed that the double increase of light intensity resulted in about eight-times increase of aerosol mass when the ambient air quality was favorable for aerosol formation. The aerosol mass was more sensitive to the change of light intensity than ozone formation.

The initial conditions that the initial concentration of NO_x was relatively low, and the concentration ratio of toluene/NO_x was relatively high, were considered to encourage the formation and growth of aerosols for groups A and C.

4. SUMMARY

The photochemical reaction of Seoul ambient air was observed in indoor smog chambers from September 2003 to June 2004. The effects of initial particle number concentration and light intensity were characterized using twin chambers. Each effect on the photochemical smog was classified into four groups, based on the variation of particle number concentration during the irradiation. The formation of ozone and aerosols during the irradiation seemed to be affected directly by the initial particle concentration, but conditionally by the light intensity. The effect of light intensity was appeared when the air quality was favorable to cause photochemical smog. The aerosol formation was highly correlated with the ozone formation [4]. The reduction of aerosols might cause adverse health effect due to the increase of ultrafine particles. However, it could contribute to suppress the growth of existing particles. The effect of light intensity was well represented in terms of the ratios between twin chambers for the same experiment.

ACKNOWLEDGEMENTS

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