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A study on the formation of photochemical air pollution and the allocation of a monitoring network in Busan

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Abstract−The characteristics of concentration variations for dust, O_3, and its precursors in Busan, South Korea were analyzed on the basis of pollution data from 19 stations during 2005. The objectives of these analyses were (i) to observe the ozone precursor concentrations under various conditions, (ii) to examine the mechanism of high [O_3] episode development, (iii) to examine the formation of photochemical aerosols, (iv) to observe the spatial distribution of high [O_3] occurrence over time, and (v) to observe the spatial distributions of temperature and wind speed over the whole area of Busan on high [O_3] episode days. The ratio of initial [NO_2] to initial [NO], O_3 dosage, and O_3 formation/hazard potential were established as relevant parameters on which to base allocation of monitoring stations according to each regional type, and criteria based on these parameters were determined for reallocating stations over the Busan area according to various regional types based on monitoring purposes. It was found that the current allocations of stations for investigating photochemical pollution do not reflect the areas where high O_3 occurs and areas where it is desirable to measure O_3 and its precursors flowing out of the target area. Therefore, based on these criteria, reallocated monitoring stations according to each regional type were suggested.

Key words: Ozone, Precursor, VOCs, Nitrogen Oxides, Photochemical Air Pollution, Monitoring Network, Allocation of Photochemical Monitoring Station

INTRODUCTION

Since the ozone concentrations in Busan, South Korea have been persistently increasing in recent times and the frequency of concentrations exceeding acceptable short-term environmental criteria has shown an increasing trend [1], continuous surveillance of photochemical pollutants and their precursors such as nitrogen oxides (NOx) and volatile organic compounds (VOCs) is necessary to establish various policies and strategies for reducing secondary air pollution [2,3]. The monitoring network for air pollution surveillance in Busan involved 19 stations in 2005, encompassing 5 different kinds of land use (Fig. 1).

The network, consisting with 10 stations in residential areas, 3 in industrial areas, and 2 each in commercial, green land, and roadside areas, has been operated to monitor environmental criteria pollutants, such as SO_2, CO, NOx, particulate matter (PM_{10}, ≤10 μm) and O_3, as well as meteorological factors including wind speed, wind direction, temperature, etc. In addition, roadside stations additionally measure Pb, $PM_{2.5}$ (≤2.5 μm), hydrocarbons (HC), and traffic volume. Also, the photochemical pollution network operates 5 stations belonging to Types I to IV and continuously monitors various representatives of VOCs.

As secondary air pollution has become a major environmental problem, it has been considered that existing stations for monitoring the primary air pollution should also monitor $PM_{2.5}$, O_3 and its precursors such as VOCs, which may have health impacts [4]. The photochemical recycling reactions of O_3, NO, and NO_2 have generally been explained by Leighton's [5] Eqs. (1) and (2) as a daytime inter-conversion process.

$$NO+O_3 \rightarrow NO_2+O_2 \quad (1)$$

$$NO_2+h_\nu+O_2 \rightarrow NO+O_3 \quad (2)$$

When radicals such as RO_2 and HO_2 are present in the atmosphere, NO is converted to NO_2 according to Eqs. (3) and (4) (Fig. 2), and the consumption of ozone by reaction (1) is reduced.

$$NO+RO_2\cdot \rightarrow NO_2+RO\cdot \quad (3)$$

$$NO+HO_2\cdot \rightarrow NO_2+HO\cdot \quad (4)$$

Monitoring stations for photochemical pollutants are classified into 4 categories or types on the basis of the monitoring objectives; (I) to measure the concentration of ozone and its precursors flowing into a target area, (II) to measure the concentration of various precursors at sites of maximum precursor emission, (III) to measure the highest ozone concentration in a target area, and (IV) to investigate ozone and its precursors flowing out of a target area.

In this study, initial concentration ratios of [NO_2]/[NO], O_3 dosage was defined as (daily maximum 1hr average O_3 concentration over 100 ppb)×[frequency(duration in hrs) over 100 ppb], and O_3 formation/hazard potential [(initial concentration ratios of [NO_2]/[NO])×O_3 dosage] were devised as parameters to be determined and developed into a criterion for allocating stations according to the 4 types of monitoring objectives described above. The first parameter is related to the emission of precursors and the potential for generating ozone. The second parameter is provided to express the dam-

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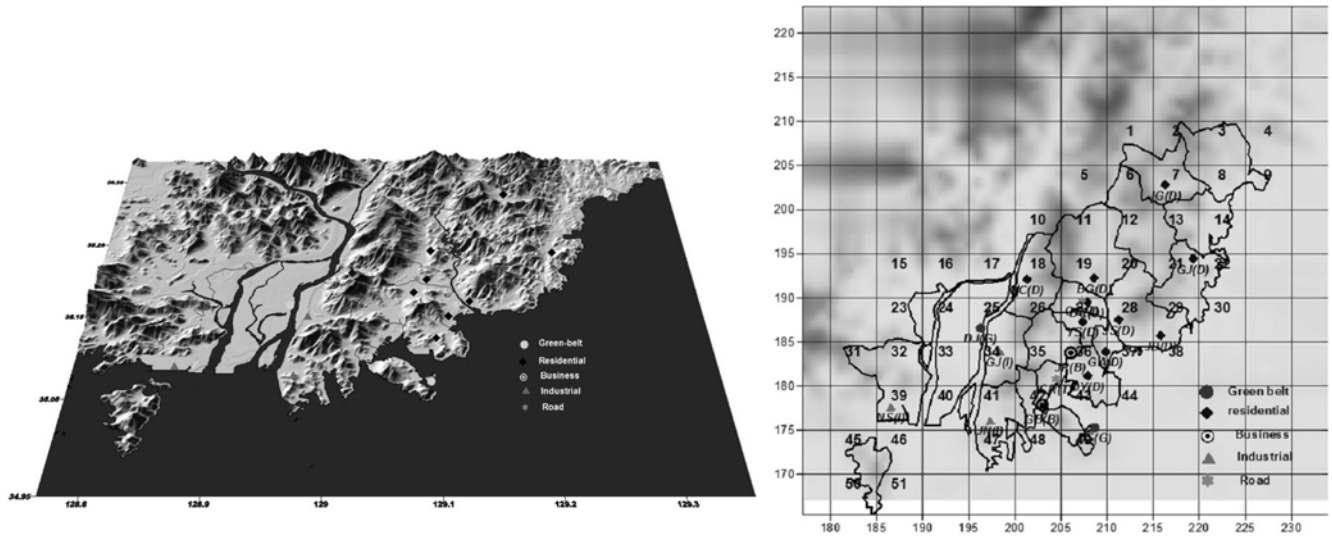

Fig. 1. Current network for monitoring air quality in Busan, 2005.

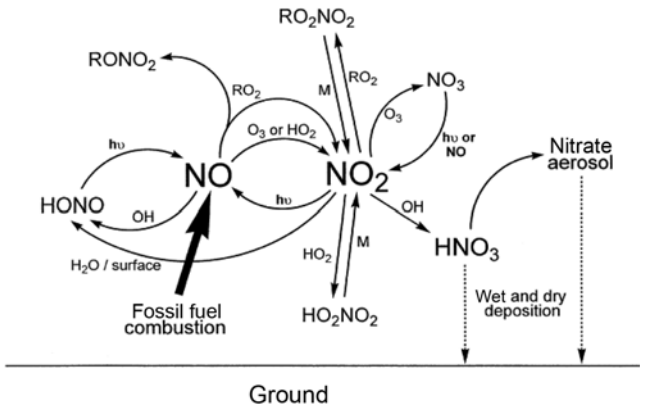

Fig. 2. Daytime inter-conversions of oxidized nitrogen compounds.

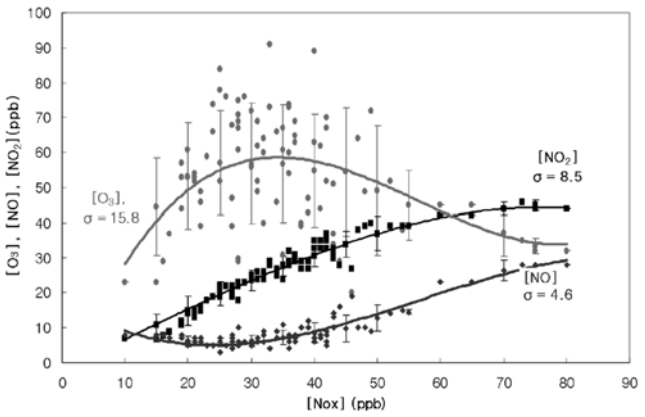

Fig. 3. Variation of 1 hr average concentration of O_3, NO, and NO_2 with [NOx] for high ozone days in Busan, 2005.

age or hazard potential due to high ozone events. The third parameter expresses the combined effect of both previous parameters through a product of the two parameters. Thus, the appropriateness of allocating stations for each current category was examined and then, in terms of criteria based on these three parameters, a desirable design method was proposed for a new monitoring network for photochemical pollution in Busan.

CHARACTERISTICS IN THE VARIATION OF OZONE PRECURSORS

Research on the distribution characteristics of precursors and their contribution to ozone formation is proposed to resolve the problems of monitoring high concentrations of secondary pollution [6,7], and the necessities for reconstruction of the air pollution monitoring network are also proposed to put emphasis on regular surveillance of secondary pollutants. To understand the contribution of precursor NOx to high ozone events under consideration of Leighton's NOx cycle (Fig. 2), the variations of 1hr average NO, NO_2, and O_3 concentration versus [NOx] ranges are displayed in Fig. 3 using pollution data collected in the daytime (09:00-17:00) from 16 stations in 2005 when $[O_{3(1hr)}]$ exceeded 100 ppb at one or more stations. Fourteen among 16 stations were selected under consideration of frequent occurrence of high O_3 events. Thus, $[O_3]$ ranged from 20 to 90 ppb.

[NO] ranged from 5 to 30 ppb and $[NO_2]$ from 10 to 40 ppb for ozone episode to occur, and $[O_3]$ appeared to increase only when $[NO_2]$ increased and [NO] was lower than the $[NO_2]$ level, or $[O_3]$ increased with the $[NO_2]/[NO]$ ratio. The standard deviations of the $[O_3]$ curve were calculated for each [NOx] interval of 10 ppb. In order to investigate the influence of NOx concentration on the $[O_{3(1\,hr)}]_{max}$ in the initial stages (06-09 A.M.) of the daily photochemical reaction under natural conditions, without severe movement and mixing of the precursors, the relationships $[O_{3(1\,hr)}]_{max}$ vs [NO] and $[O_{3(1\,hr)}]_{max}$ vs $[NO_2]$ were plotted (Fig. 4) using data at calm conditions ($\bar{u} \leq 2$ m/s), from stations located in basin areas with restrictions on the horizontal transport of pollutants.

In the atmosphere near the surface in Busan, high concentrations of ozone formed at [NOx] levels of about 20-30 ppb, and $[O_3]$ reached about 55 ppb when the curves of $[NO_2]$ and [NO] intersected. Also, $[NO_2]$ comprised the bulk of the [NOx] when $[O_{3(1\,hr)}]_{max}$ was about

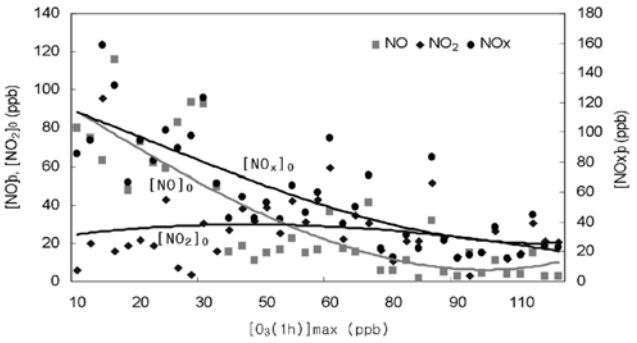

Fig. 4. Relationship between $[O_{3(1\,hr)}]_{max}$ and initial (06-09A.M.) [NOx] on ozone episode days ($[O_{3(1\,hr)}]_{max}$≥100 ppb) in Busan, 2005.

90 ppb. $[O_{3(1\,hr)}]_{max}$ was greater than or equal to 55 ppb when $[NO_2]$≥[NO], while $[O_{3(1\,hr)}]_{max}$<55 ppb when $[NO_2]$<[NO]. These observations indicated that the O_3 forming reaction expressed in Eq. (2) was prevalent in Busan; however, the existing O_3 was partially consumed in the oxidation of NO as shown in Eq. (1) and Fig. 3, if [NOx] was largely high due to increased [NO]. This point may mean that the contribution of oxygenated hydrocarbons to the oxidation of NO is also restricted during ozone buildup under increased [NO] condition. The concentration distributions of NOx and VOC as precursors of ozone near sunrise (the initiation of photochemical reactions), the ratio of [VOC] to [NOx], and the $[O_{3(1\,hr)}]_{max}$ for each station on ozone episode days ($[O_{3(1\,hr)}]_{max}$≥100 ppb) in Busan are displayed in Fig. 5.

This Figure shows that high level ozone mainly forms when 20≤$[NOx]_o$≤70 ppb, 200≤$[VOC]_o$≤1,500 ppb, and $[VOC]/[NOx]_o$≥8, which means that high concentrations of ozone built up when ozone consumption was reduced by the contribution of oxygenated HC serving to increase the oxidation of NO (Eqs. (3) and (4)).

Comparing these results with the typical result of Dodge [8] using the empirical kinetic modeling approach (EKMA), the occurrence of an ozone episode in Busan corresponded to conditions near the curved regions of the ozone isopleths which are close to the NOx-limited condition, although these data might not be representative of the whole area of Busan. This observation was in contrast to the situation regarding atmospheric conditions in 1981, reported by Park

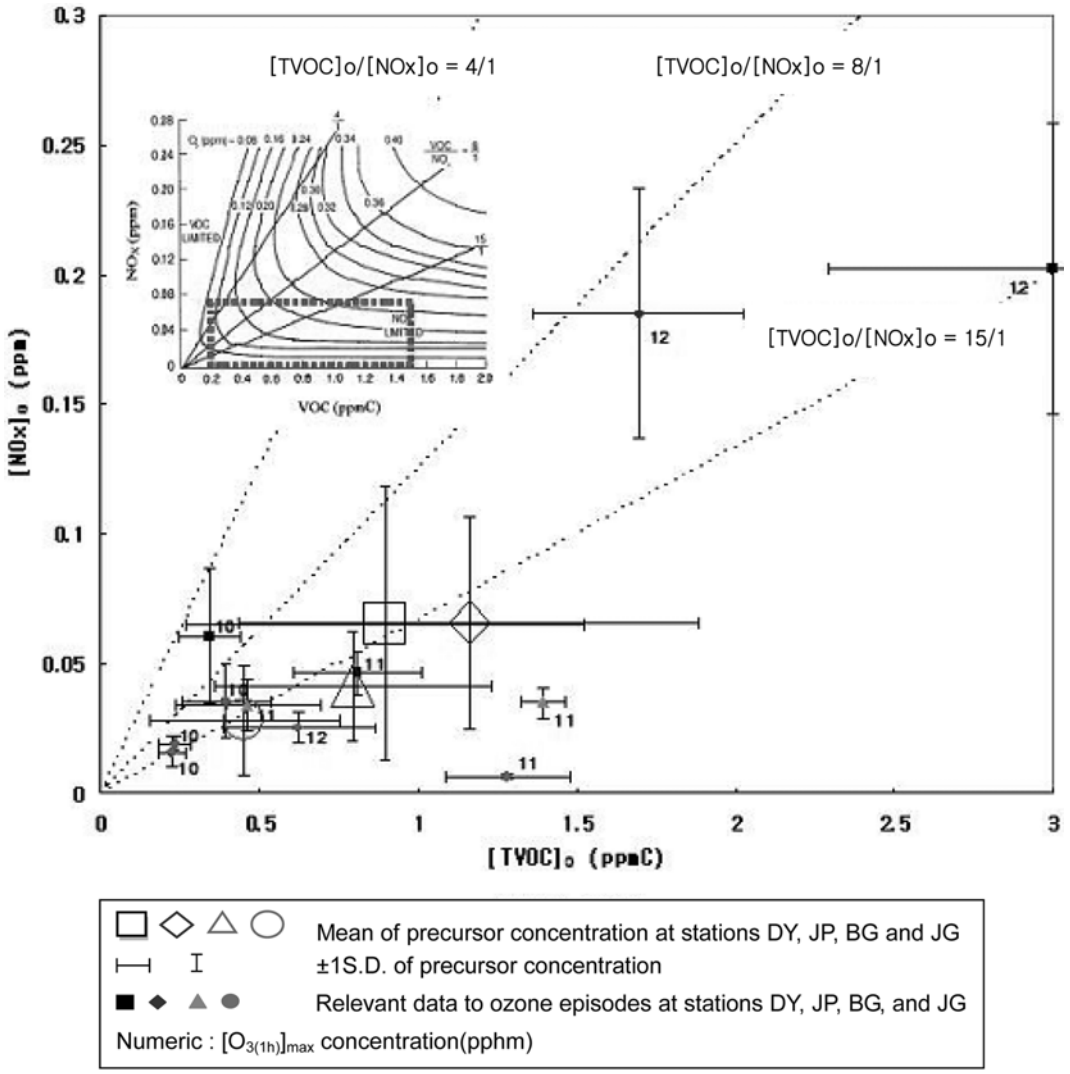

Fig. 5. Dependence of $[O_{3(1\,h)}]_{max}$ on the concentration of $[NOx]_o$ and $[VOC]_o$ and the ratio of $[VOC]_o/[NOx]_o$ in Busan, 2005.

[9], in which an ozone episode ($[O_{3(1\,hr)}]_{max} \geq 100$ ppb) could have been avoided if 60% of the non-methane hydrocarbons ($[NMHC_{(3\,hr)}]$) and 20% of $[NOx_{(3\,hr)}]$ during 6:00-9:00A.M. were reduced. This contrast appeared to be caused by small variations in the distribution of the precursors' concentrations probably due to the significant change in vehicle technology leading to emission change.

THE OCCURRENCE OF AN OZONE EPISODE AND THE FORMATION OF PHOTOCHEMICAL AEROSOL

In this part of the study, the characteristics of temperature and wind speed distribution on ozone episode days and the spatial variation of ozone concentration over the time of the episode are examined. Temperature isopleths and the distribution of wind speed during 09:00-15:00 on ozone episode days ($[O_{3(1\,hr)}]_{max} \geq 100$ ppb) in Busan (Fig. 6) revealed that: (i) ozone episodes mainly took place at relatively low wind conditions ($\bar{u} \leq 4$ m/s) in most areas except a southeastern coastal area, and (ii) minimum temperatures of 24 °C were recorded along coastal areas and showed gradual increases going inland. The wind speed of 4 m/s in Busan was regarded as relatively low wind condition considering the general climatology expressed in wind roses [10]. This illustrated that ozone episodes in Busan occurred when advection air currents carrying precursors over relatively complex terrain were weak in most areas except the southeastern coastal area. In other words, photochemical reactions largely occurred under stable conditions in a basin or a valley terrain where horizontal air movement was restricted.

In a northeastern suburban area, high concentrations of ozone occurred most often at 11:00 LST, and ozone episodes occurred after 13:00 LST over nearly the entire Busan area (Fig. 6(b)). In the Busan air basin, ozone episodes took place first along the coastal areas and their neighboring suburban areas, and there appeared to be a delay in the occurrence time (at about 16:00 LST) towards the central part of the city. The reason for the delay in the central urban area, which has a basin-like terrain, appeared to be due to the large amount of ozone consumed in the oxidation of NO, which may reach high levels in a central urban area.

Table 1. Correlation coefficients between various pollutant concentrations during daytime for ozone episode days (n= 87)

	PM_{10}	$PM_{2.5}$	O_3	NO_2	NO	NO_x	O_x
PM_{10}	1.00						
$PM_{2.5}$	0.90	1.00					
O_3	0.34	0.33	1.00				
NO_2	0.77	0.65	0.10	1.00			
NO	0.28	0.25	−0.50	0.51	1.00		
NO_x	0.68	0.58	−0.12	0.94	0.78	1.00	
O_x	0.70	0.64	0.80	0.65	0.03	0.50	1.00

A significant portion of $[PM_{10}]$ was presumed to be photochemical aerosol because $[PM_{10}]$ values simultaneously exceeded the environmental criteria at some monitoring stations where the $[O_3]$ frequently exceeded environmental criteria. Thus, the correlation between fine dust and gaseous pollutants on high ozone days was analyzed for the daytime (09:00-17:00), May-Sept., 2005 in order to understand the characteristics of secondary aerosol formation by photochemical reactions [11,12], and the results expressed in Table 1.

The correlation coefficient between $[PM_{10}]$ and $[PM_{2.5}]$ was very high (r=0.90 for n=87) and those between O_3 and PM_{10} or $PM_{2.5}$ were relatively low but, on the other hand, those between oxidants, $[Ox\ (=NO_2+O_3)]$, and $[PM_{10}]$ or $[PM_{2.5}]$ were high (r=0.64 or 0.70 for n=87). The relatively low correlation of PMs with O_3 appeared to be due to the time delay between the occurrence of peak concentrations for O_3 and fine dust, but the relatively high correlation with Ox suggests the high probability of the subsequent formation of secondary aerosols by photochemical reactions. To examine this relation in more detail, the results of a regression analysis between Ox and fine dust concentrations for ozone episode days are shown

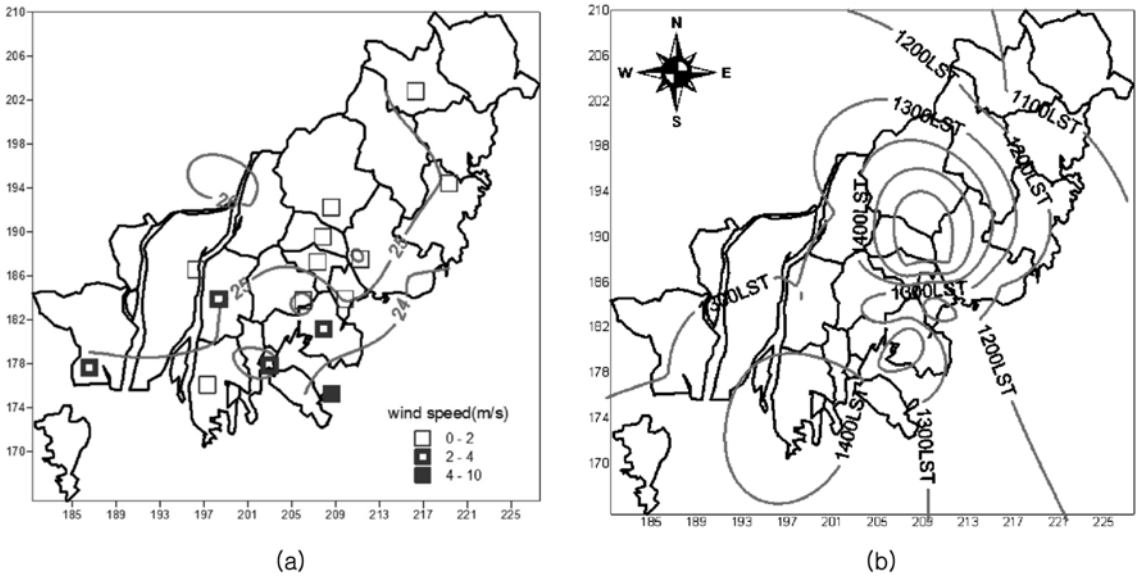

Fig. 6. (a) Temperature and wind speed distribution in the daytime, and (b) isopleth of peak ozone occurrence time for ozone episode days during May-Sept., 2005.

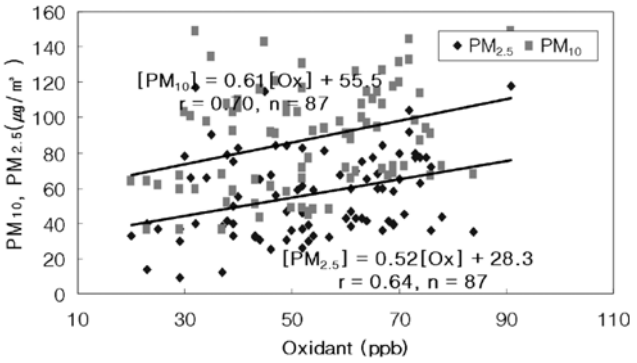

Fig. 7. Relationship between Ox and dust concentrations.

in Fig. 7, clearly showing the positive influence of [Ox] on the [PM_{10}] and [$PM_{2.5}$]. In the linear relation [PM]=a[Ox]+b, "b" may indicate the primary aerosol, representing a major portion of the dust when [Ox] is negligible, and "a[Ox]" is presumed to be the secondary aerosol formed when [Ox] increases.

Fig. 8 shows the results of regression analysis between [$PM_{2.5}$] and [PM_{10}] for ozone episode as well as non-episode days at stations in industrial and commercial areas in 2005. The coefficient of determination was very high (R^2=0.94 for n=216) on high ozone days at station JN located in an industrial area; however, that for station YS in a commercial area turned out to be significantly low. Also, the large slope value (1.3) and the small intercept value (near zero) at JN suggested that a significant portion of the PM_{10} consisted of $PM_{2.5}$, while the small values of the determination coefficient (0.31), slope (0.65), and intercept (34.4 μg/m^3) for the YS site in a central urban commercial area could be partially attributed to the complicated dust origins, including fugitive dust, car exhaust dust, and photochemical aerosols. For non-episode days, the linear regressions between PM_{10} and $PM_{2.5}$ at the sites YS (commercial area) and JN (industrial area) had large intercept values and small determination coefficients (R^2) of 0.27 and 0.24 for n=359, respectively, and did not necessarily indicate that there were any linear functional relationships here.

ALLOCATION OF MONITORING NETWORK FOR PHOTOCHEMICAL POLLUTION SURVEILLANCE

The monitoring network for photochemical pollution surveillance in Busan operates 5 stations belonging to 4 types, (Fig. 13(a)). The operating objective of photochemical pollution monitoring network is different from that of "Urban air quality monitoring network" and these networks are operated independently.

In this part of the study, methods for the reallocation of the monitoring stations were examined through the establishment of criteria for their allocation and re-estimating the utility of the current station allocations according to each type using the criteria. The allocation criteria were established in terms of the range of each parameter such as the ozone formation/hazard potential ratio, O_3 dosage, and the [NO_2]/[NO] ratio. Ozone events higher than 55 ppb occurred when $[NO_2]_o > [NO]_o$, while [O_3] was reduced because part of the already produced O_3 was consumed by NO oxidation when $[NO_2]_o < [NO]_o$ during the 6:00-9:00A.M. time period and, thus, the ratio $[NO_2]_o/[NO]_o$ was taken as a parameter expressing relative precursor emissions and the potential for ozone formation. This parameter was used in determining the appropriate location for type II stations to

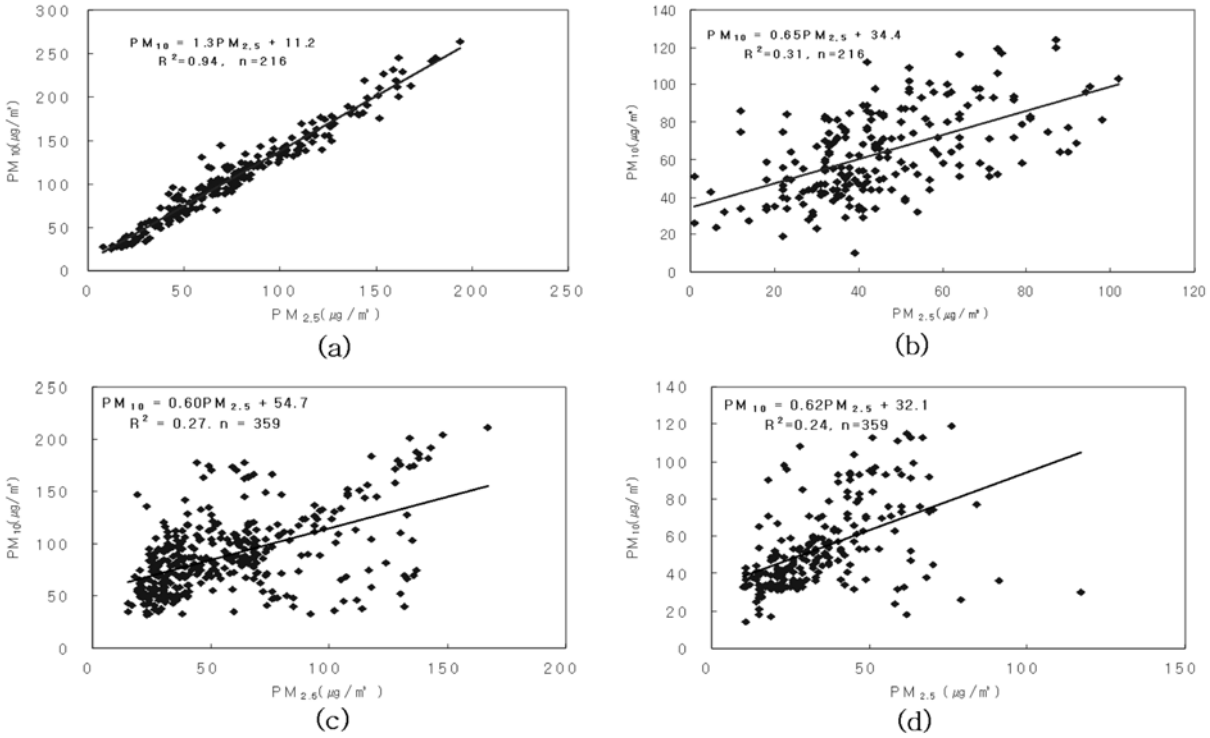

Fig. 8. Regression analysis between [$PM_{2.5}$] and [PM_{10}] for ozone episode days ($[O_{3(1\,hr)}]_{max} \geq 100$ ppb) at sites (a) JN and (b) YS and those for non-episode days at sites (c) JN and (d) YS in 2005.

be operated in areas of high precursor emissions. Ozone dosage was defined as ($[O_{3(1\,hr)}]$×episode occurrence frequency in hrs) and taken as a parameter associated with the determination of type III stations to be operated in the area of the maximum ozone potential. Furthermore, a comprehensive parameter was constructed to effectively monitor photochemical pollutants (Eq. (5)) taking into consideration of NOx emissions, the potential for ozone formation and that for hazardous ozone levels.

$$P_{2nd} = \frac{[NO_2]_o}{[NO]_o} O_3 \text{ dosage} \quad (5)$$

where P_{2nd}=daily potential of ozone formation and hazard.

The values of each parameter such as $[NO_2]_o/[NO]_o$, O_3 dosage, and P_{2nd} were obtained from 19 monitoring stations when $[O_{3(1\,hr)}]_{max}$ ≥100 ppb, during May-Sept., 2005 in Busan. To set up spatial allocation criteria for a photochemical pollution monitoring network, the ratio $[NO_2]_o/[NO]_o$ was expressed on the x-axis, O_3 dosage on the y-axis, and the comprehensive parameter on the z-axis as shown in Fig. 9(a). Only 14 stations, where $[O_{3(1\,hr)}]$ frequently exceeded 100 ppb, are expressed in Fig. 9.

Examination of the average NO concentrations for each stations

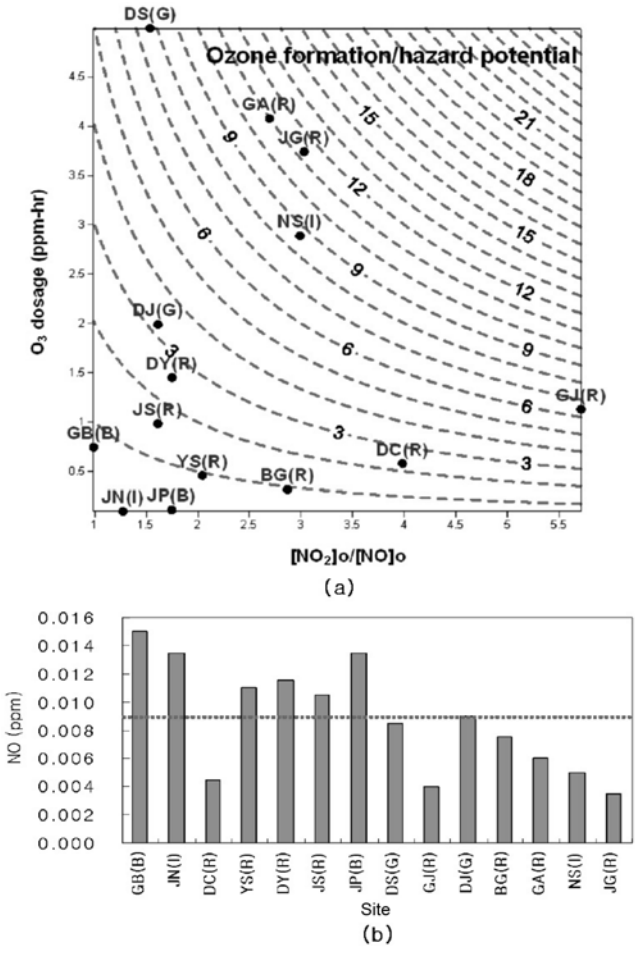

Fig. 9. (a) The relationships between $[NO_2]_o/[NO]_o$ ratio, O_3 dosage, and ozone formation/hazard potential (P_{2nd}) and (b) the distribution of NO concentration at various monitoring stations on ozone episode days in Busan during May-Sept., 2005.

where the $[O_3]$ frequently exceeded 100 ppb during May-Sept., 2005 (Fig. 9(b)) showed that stations DY(R), GB(B), JN(I), JP(B), JS(R) and YS(R), corresponding to the conditions (a) ozone formation/hazard potential≤3, (b) $1 \le [NO_2]_o/[NO]_o \le 2$, and (c) O_3 dosage≤1.5 showed relatively high [NO]≥9 ppb (The letters in parentheses after station names indicate land use: B for business, I for industrial, and R for residential.). As a result, O_3 dosage corresponded to a low level because consumption of produced O_3 was performed due to high NO emissions. Thus, these stations were classified into type II areas (Fig. 11).

The stations DS(G), GA(R), JG(R), corresponding to the conditions (a) $1.5 \le [NO_2]_o/[NO]_o \le 3$, and (b) O_3 dosage≥3.5, have relatively high ozone dosage compared with other stations and, in particular, GA(R) and JG(R) stations showed the highest potential (≥10) of ozone formation/hazard. Thus, GA and JG stations and their surrounding areas were classified as type III areas. The DS(G) station was operated for background concentration monitoring and had conditions of (a) $[NO_2]_o/[NO]_o \le 2$, which was relatively low, on ozone episode days and (b) [NO] ≒ 9 ppb, which is relatively higher than those for GA(R) and JG(R) stations belonging to same geographical area, but was similar to the average level of [NO] for overall stations. Thus, DS(G) station was selected as a type I station.

To understand the episode forming process including precursor movement during high ozone events at DS(G) station, the diurnal variation of wind direction (WD), wind speed (WS), $[O_3]$, [NOx], [NO], $[NO_2]$, and $[NO_2]/[NO]$ ratio are displayed in Fig. 10. Considering the diurnal variation of meteorological factors such as wind direction and speed before and after ozone episode days ($[O_{3(1\,hr)}]_{max}$> 100 ppb) at DS(G) station, which was located near a beach, shown in Fig. 10(a), it was considered that the transport and diffusion of pollutants from inland and/or marine sources, when northerly and easterly winds ($\bar{u} \le 3$ m/s) blew at dawn on ozone episode days, contributed to the increase of NOx concentrations (Fig. 10(b)). In particular, the concentration of the primary pollutant NO was relatively high compared with $[NO_2]$, so the ratio $[NO_2]_o/[NO]_o$ near sunrise became low (Fig. 10(c)). Thus, ozone precursors released from inland sources and ships, along with NO_2 and ozone which had been formed in daytime on previous days in inland areas, including urban centers, were transported seaward by land breezes at night, and then re-transported by sea breezes towards land after sunrise [13,14]. As a result, Fig. 10 shows the effect that the ratio $[NO_2]_o/[NO]_o$ decreased and the concentrations of O_3 and its precursors increased when sea breezes re-circulated them from sea to land (WD=120-140°).

The GJ(R) station with $[NO_2]_o/[NO]_o$ 5 and O_3 dosage 1.5 has relatively low NO emissions compared to other stations (Fig. 9(b)), and a somewhat low O_3 dosage, but showed an ozone formation/hazard potential as high as 6.5 (Fig. 9(a)), indicating a characteristic of the station that NO emissions alone did not suggest. Thus, on the basis of the above results, the criteria for determining the allocation of the various types of stations for photochemical pollution surveillance are presented in Table 2 and Fig. 11. As a refinement of the classification and application range of these criteria for photochemical pollution stations, the ozone dosage boundary criterion between types II & IV and I & III was set at 1.0 ppm·hr, and the range of $[NO_2]_o/[NO]_o$ was classified for each regional type with the consideration that the $[NO_2]$ and [NO] for each station near sun-

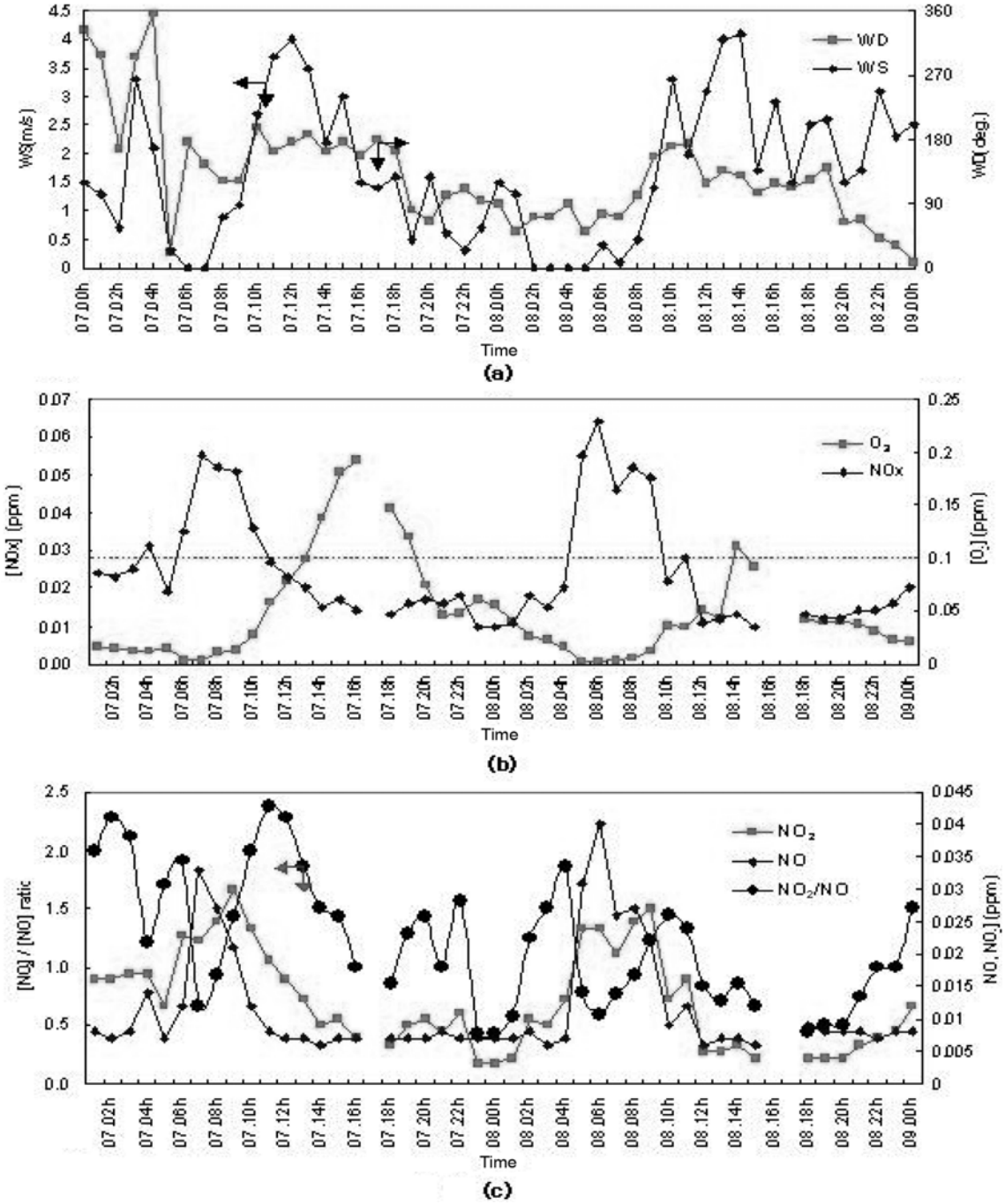

Fig. 10. Diurnal variation of (a) wind (WD, WS), (b) [O_3], [NO_x], and (c) [NO], [NO_2], and [NO_2]/[NO] ratio with time at DS(G) station from 7 to 8 Aug., 2005.

Table 2. Criteria for allocation of monitoring stations for photochemical pollution

Type	Criteria		
	O_3 formation·hazard potential (ppm·hr)	$[NO_2]_0/[NO]_0$ ratio	O_3 dosage (ppm·hr)
I	potential≤10	1.0≤ratio≤2.0	O_3 dosage≥4.5
II	potential≤2	1.0≤ratio≤2.0	0<O_3 dosage≤1.0
III	9≤potential≤16	2.5≤ratio≤3.5	3.5≤O_3 dosage≤4.5
IV	potential≤6	5.0≤ratio≤6.0	0<O_3 dosage≤1.0

rise on ozone episode days were essential factors reflecting the emission and ozone forming potential of the precursors in an area.

Special criteria ranges for each parameter and regional type were set up within the minimum section of parameters' values with the cost for founding and operating stations as a practical limiting factor. Also, when the values of the parameters for a station deviated from the established range, a station with values close to the established ranges of the parameters for each regional type was designated as an appropriate station for the type.

The allocated areas for the photochemical pollution monitoring

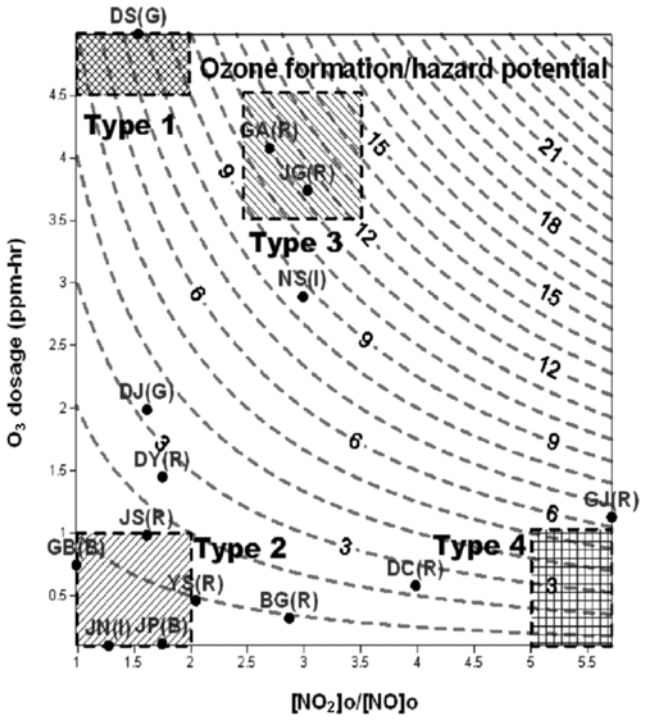

Fig. 11. Nomogram of allocating the monitoring stations for photochemical pollution.

stations for each regional type, determined by using the above nomogram (Fig. 11) and criteria (Table 2), are shown in Fig. 12. The allocated area was selected by considering an area which simultaneously satisfied the isopleths of each parameter criteria for a certain regional type. Fig. 12(a) shows that type I monitoring stations were located in coastal areas where the criteria ranges were simultaneously satisfied for the $[NO_2]/[NO]$ ratio, ozone dosage, and the ozone formation/hazard potential. Types II and III monitoring stations, where ozone precursors emissions are somewhat large and O_3 dosage values are high, corresponded to the region including station DS(G), and Figs. 12(b) and 12(c) suggest that DS(G) station can also be operated as a type I station operated to monitor O_3 and its precursors flowing into the target area near sunrise, because DS(G) is located in an outer urban area in the upwind direction in the morning and could monitor the movement inland near sunrise of precursors and O_3 which had been transported seaward during the previous night.

Type II monitoring stations were allocated in the harbor area and its surroundings, the urban center, and industrial areas where emissions of precursors were large (Fig. 12(b)). Since ozone episodes frequently occur in coastal areas of Busan, the type II stations should be located in coastal areas and places located in surrounding inland where emissions of ozone precursors from land and sea can be monitored. The existing air pollution monitoring stations, such as GB(B), JN(I), JP(B), YS(R), and JS(R), belonged to above mentioned area, and it was feasible to classify them as type II stations.

Type III stations, to be designated at sites where the highest ozone concentration occur, were allocated separately in a coastal area and a city outskirts (Fig. 12(c)). The JG(R) station located in city outskirts surrounded by mountains exhibited that ozone episodes around the station occur from the influence of basin terrain and the local pollution characteristics, rather than the influence by the precursors' transport and diffusion. Thus, it appears more appropriate to select GA(R) as a type III station where the influence of precursors' transport and diffusion was reflected in the ozone formation and ozone episodes frequently occurred.

There was no existing station which simultaneously satisfied the criteria of $[NO_2]_o/[NO]_o$, O_3 dosage, and ozone formation/hazard potential in the area where type IV stations could be designated for measuring the concentrations of ozone and precursor flowing outward from target areas (Fig. 12(d)). Though it seemed to be reasonable that the station GJ(R) be regarded as a type IV station because the criteria of this station were closest to those of type IV stations, however, it appeared to be more appropriate to allocate type IV stations to the northern part of Busan where ozone and its precursors flowed outward from the target area under the influence of daytime winds.

On the basis of the discussion above, current and reallocated maps of the monitoring stations in Busan were compared (Fig. 13). The current map was fundamentally made to allocate stations for (i) the investigation of precursor concentrations, (ii) clarifying the mechanism(s) of ozone formation, and (iii) the surveillance of ozone hazards. The reallocated map was created by allocating stations for each regional type with consideration of the criteria ranges of $[NO_2]_o/[NO]_o$, O_3 dosage, and ozone formation/hazard potential. Through the comparison between the suggested future reallocation and the current allocation maps, it was observed that the latter did not appear to properly reflect the high ozone occurrence areas and the zones from which ozone and its precursors flowed outward.

CONCLUSIONS

As a result of observations on the characteristics of ozone formation and precursor behavior and the establishment of useful criteria for allocating the monitoring station sites on the basis of meteorological and environmental data from 19 stations during 2005 in Busan, the following conclusions were drawn:

1) On high ozone days ($[O_{3(1\,hr)}]_{max} \geq 100$ ppb) in Busan, [NOx] in the near surface atmosphere was about 20-40 ppb. Furthermore, $[O_{3(1\,hr)}]_{max}$ was larger than or equal to 55 ppb when $[NO_2]_o \geq [NO]_o$ near sunrise, but less than 55 ppb when $[NO_2]_o < [NO]_o$. This observation suggested that though NO_2 largely contributes to O_3 formation in Busan, part of the already formed O_3 was consumed by the oxidation of NO to NO_2, and if high [NOx] was present through an increase of [NO], the $[O_3]$ could be reduced or could not accumulate.

2) The formation of $[O_{3(1\,hr)}]_{max}$, indicated by the $[NO_2]_o/[NO]_o$ ratio on high ozone days during 2005 in Busan, mostly corresponded to a ratio of $[VOC]_o/[NOx]_o$ equal to or larger than 8/1 and, when plotted, near the curvature part of horizontal ozone isopleth, which was close to the NOx-limited condition. Considering a previous report by Park (1985) based on data in 1981, these observations appeared to indicate that the distribution of HC and NOx concentrations has varied to some extent in the last 2.5 decades before 2005 and resulted in a different situation to control photochemical pollution from that in the early 1980s.

3) In Busan, high ozone concentrations occurred first in the northeastern part of city outskirts at 11:00 LST, expanded to cover al-

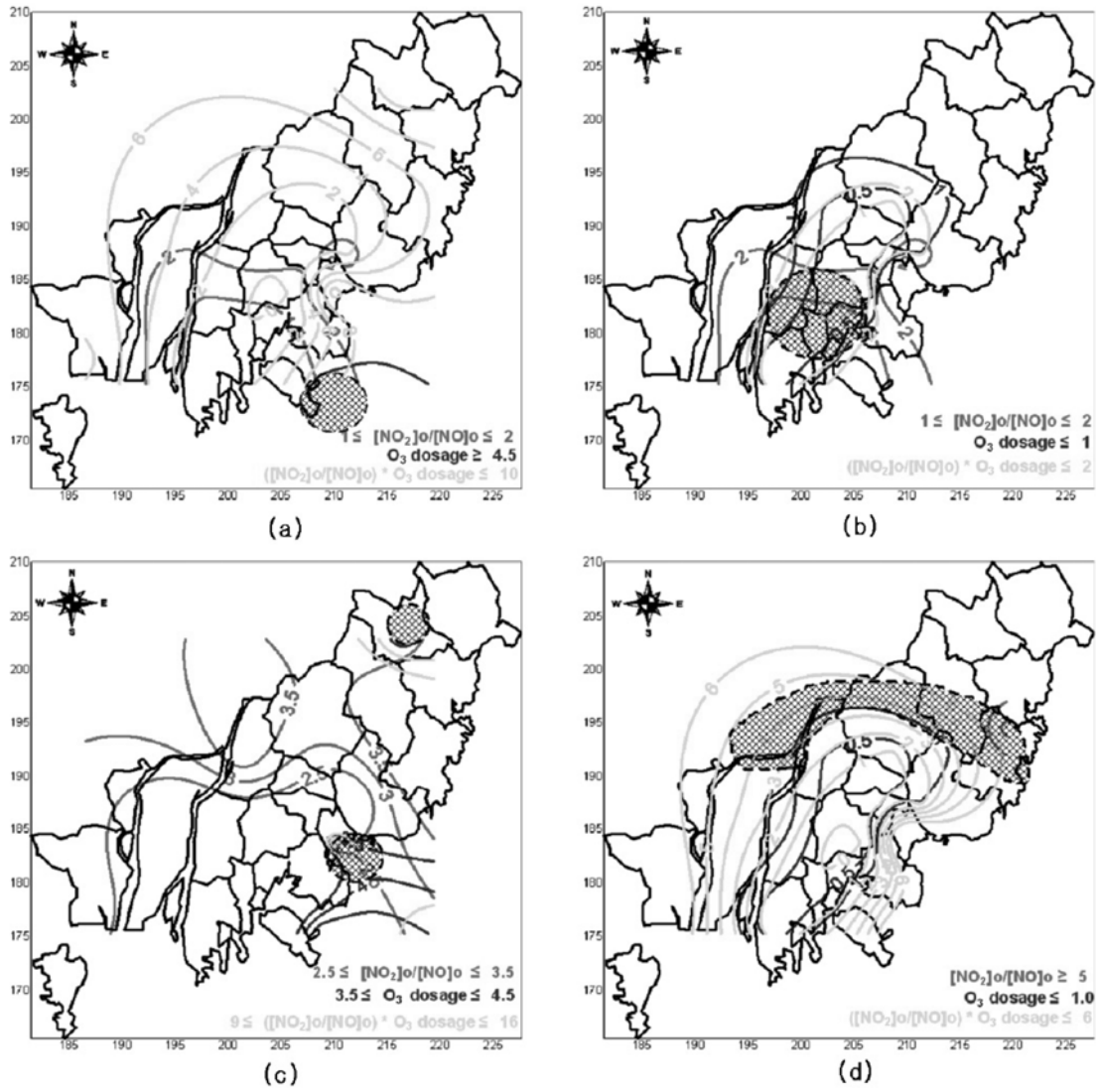

Fig. 12. Areas of monitoring stations for photochemical pollution in Busan: types (a) I, (b) II, (c) III, and (d) IV.

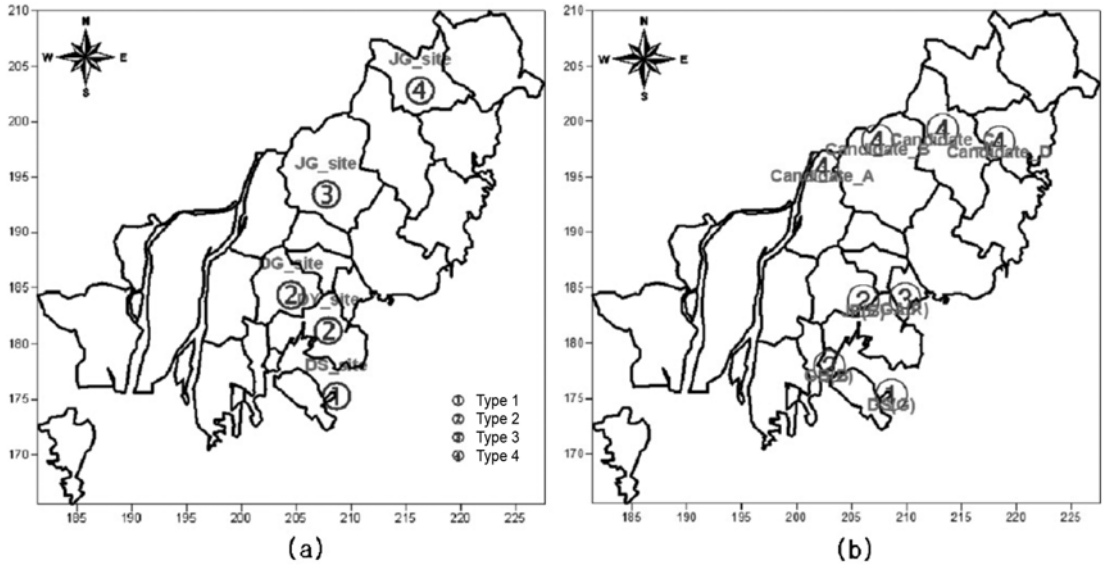

Fig. 13. Monitoring stations for photochemical pollution in Busan: (a) current, and (b) reallocated.

most the entire area after 13:00 LST, and occurred in the urban central area at 16:00 LST, with the delay of O_3 accumulation attributed to the consumption of existing O_3 by high [NO] in the central areas. Also, temperature showed a pattern of increase starting in the coastal areas and then spreading to the inland areas. Photochemical reactions leading to an ozone episode appeared to occur at stable conditions in basin or valley terrains, where horizontal air movement was limited, when advection carrying the precursors of ozone did not flow through the complex terrain of Busan.

4) During high ozone episodes, the relation between PM_{10} and $PM_{2.5}$ showed very high correlation (r=0.90 for n=87), and a relatively high correlation (r=0.64-0.70) was found between oxidants (NO_2+O_3) and aerosols (PM_{10} or $PM_{2.5}$). These facts suggested that high ozone and aerosols are formed as a result of photochemical reactions.

5) In this study, the criteria to allocate monitoring stations for each regional type were established in terms of the range of three parameters: $[NO_2]_o/[NO]_o$, O_3 dosage, and ozone formation/hazard potential. The initial ratio of $[NO_2]$ to [NO] reflects the emission of precursors; the ozone-forming potential, ozone dosage implies the hazard or impact due to high ozone levels, and the ozone potential parameter consists of the above two parameters and indicates the potential of ozone formation and its hazards. From the comparison of the current sites and the future allocation of stations for each regional type, using the allocation criteria established in this study, it appears that current allocation did not properly reflect the areas producing high ozone and the areas where O_3 and its precursors, flowing out of the target area, should be monitored.

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