OZP-OZONE PROBLEMS

**Third International Symposium
on
AIR QUALITY MANAGEMENT
at Urban, Regional and Global Scales
&
14 th IUAPPA Regional Conference
26-30 September 2005
Istanbul, Turkey**

OZONE PROBLEMS

INTERACTION PATTERNS OF SURFACE OZONE WITH NO$_x$ AND NMHC IN EIGHT CITIES OF AICHI AND MIE PREFECTURES, JAPAN

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ABSTRACT

Interaction patterns between surface ozone and its precursors (nitrogen oxide (NO$_x$) and reactive non-methane hydro carbon compounds (NMHC)) in the local scale have been statistically analyzed for eight different cities of Aichi and Mie prefectures of Japan. Selected monitoring sites represented different land habitats namely coastal-industrial (Yokkaichi, and Tsu), inland urban sites (Nagoya center, Toyota city, Toyohashi, and Okazaki), mountain-base urban (Nabari), and coastal resort city (Toba). Hourly raw ambient data on air criteria pollutants (1993-2003) of Air Quality Authority of Mie and Aichi Prefecture were used to investigate the relationships of ozone with precursors and the photochemical indicators such as NO$_2$/NO and NMHC/NO$_x$.

Decomposition analysis was done to determine the seasonally adjusted trends of the pollutants. Despite relatively low concentrations of NO$_x$ and NMHC, coastal sites experience relatively high ozone level than the inland urban sites indicating possible meteorological effects on the ozone movements and differences in ozone deposition rates. NO$_2$/NO ratio plays significant influence on ozone level of the inland sites while the influence of NMHC/NO$_x$ was significant in sites with the characteristics of high density of industries and higher population of traffic. Seasonal variations in interaction patterns show stronger relationships between ozone and precursors in the winter and weaker relationships in the summer indicating the possible meteorological effects and higher rate of pollutants dispersions in the summer. Effects of land habitats particularly the topography plays important roles in the distribution patterns of the air pollutants.

Key words: Surface ozone, Ozone precursors (NO$_x$ and NMHC), Interaction Patterns, Urban pollution, Photochemical indicators (NO$_2$/NO, and NMHC/NO$_x$)

1. INTRODUCTION

Surface level ozone formation is a complex process that is caused, under favorable photochemical conditions, by the nitrogen oxide (NO_x) and volatile organic compounds (VOC) emitted from traffic vehicles, industrial activities, and household combustions (Health Canada, 2002; Lu and Wang, 2003). Studies show that intensity of ozone production depends on the availability of NO_2 and the favorable photochemical conditions such as solar radiation and ambient temperature enhance the production of NO_2. The availability of NO_2 depends on the rate of transformation of NO_x and reactive volatile organic compounds (also called non-methane hydrocarbons) (Cooper and Alley, 2002; Sillman 1999). Interaction between ozone and precursors is mainly dominated by the production of secondary pollutant called NO_2 which subsequently undergoes photolytic reaction to produce ozone. Production of NO_2 in the atmosphere can be made by NO at the expense of available ozone or by reactive volatile organic compounds without consuming available ozone. However, chemistry of ground level ozone goes through a complex process of production and destruction cycle. Anthropogenic (traffic, industrial process etc.) and biogenic sources emits nitric oxide (NO) and reactive components of VOCs that are believed to undergo several chemical reactions (Health Canada, 2000; Lu and Wang, 2003; Cooper and Alley, 2002) to produce NO_2. The amount of ozone in a certain time and location depends on the ratio of NO_2 and NO in the air and also on the availability of these two compounds.

The ratio of NO_2 and NO plays a vital role in stabilizing the ozone level through the production as well as the destruction process (Lu and Wang, 2003; Saito *et al*., 2002). Saito et al. (2002) found that the ozone production level could be related to the ratio of NO_x and NMHC because reactive NMHCs could convert NO into NO_2 without consuming O_3. Volatile Organic Compounds (VOC) react with hydrogen-containing radicals ($HO_2\cdot$) to yield peroxy radicals ($RO\cdot$) that contribute to the production of NO_2 through a chain of intermediate reactions.

In fact, the ratio of NO_2/NO at a certain location can be considered as an indicator of the potential of ozone production. Higher ratios of NO_2/NO indicate higher levels of ozone production, and low ratios indicate the higher potential for ozone destruction. In addition, the relationship between NO_x and NMHC also influences the ozone production processes where the ratios $NMHC/NO_x$ could also be used as photochemical indicator to control peak ozone level at a certain location (Cooper and Alley, 2002). Meteorological factors like wind speed and direction are responsible for transporting both ozone and its precursors from its source to far distant places, but seasonal variations in ambient temperatures influence substantially on the ozone production process and its temporal behavior (Olsyzna *et al*. 1997, Aneja *et al*. 2000, and Ribes *et al*. 2004). Ambient ozone level is destroyed mainly by two ways namely, scavenging by the fresh emission of NO or by depositions of ozone on the soil and absorption by plant and vegetation (Fuentes *et al*., 1992; Grantz *et al*, 1997; Chang *et al*., 2002). Therefore, sites with different land topography would have effects on the ozone destruction rates.

This study aims to characterize the interaction patterns of ozone with its precursors through analyzing the pattern of NO_2/NO, $NMHC/NO_x$ level, and their correlations with ozone.

2. STUDY METHODS

2.1 Description of the Study Areas and Data Gathering

We have chosen eight different cities of the Aichi and Mie prefecture namely, Nagoya city center, Toyota city, Okazaki, Toyohashi, Yokkaichi, Tsu, Nabari, and Toba for the study. These cities (shown in the Figure 1) represents different land habitats in terms of population; land use, commercial and industrial activities such as coastal-industrial (Yokkaichi, and Tsu), inland urban sites (Nagoya center, Toyota city, Toyohashi, and Okazaki), mountain-base urban city (Nabari), and coastal resort city (Toba).
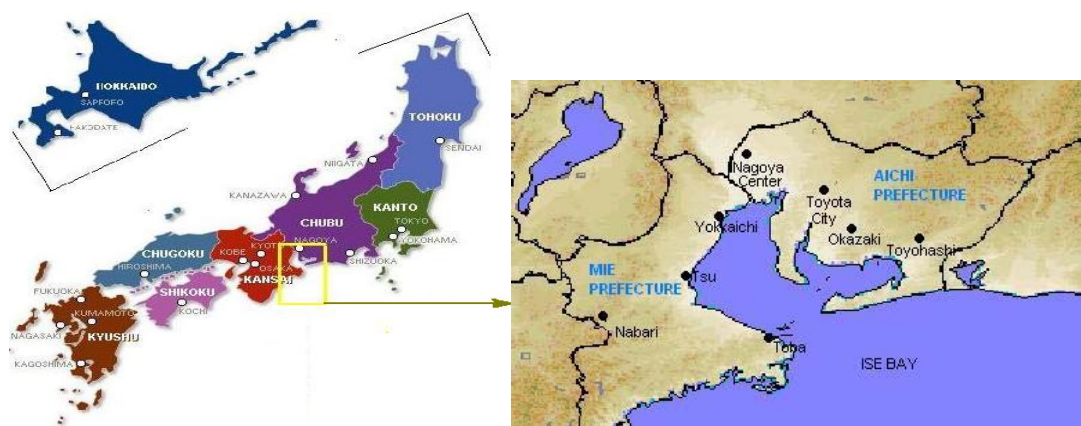

Figure 1: Maps showing Aichi and Mie Prefecture and the Approximate Locations of the Selected Monitoring Sites

Ambient air quality data of the selected monitoring stations were gathered from the Prefectural authorities of Mie and Aichi. Hourly concentration data for the period of 1993-2002 were considered for analysis. The raw data was further analyzed statistically to derive aggregated diurnal, daily, monthly, seasonal and annual values. Missing values were replaced with the 4 nearby mean values. Regression analysis of the aggregated values was done for determining the interactive characteristics of ozone and its precursors. Statistical software Minitab, MS Excel, and SPSS were used for data analysis.

3. RESULTS AND DISCUSSION

3.1 Trend Analysis of Ozone and its Precursors

Decomposition analysis of the monthly mean values of ozone was done for the periods of 1993-2002 to examine the seasonally adjusted trend as shown in Figure 2.

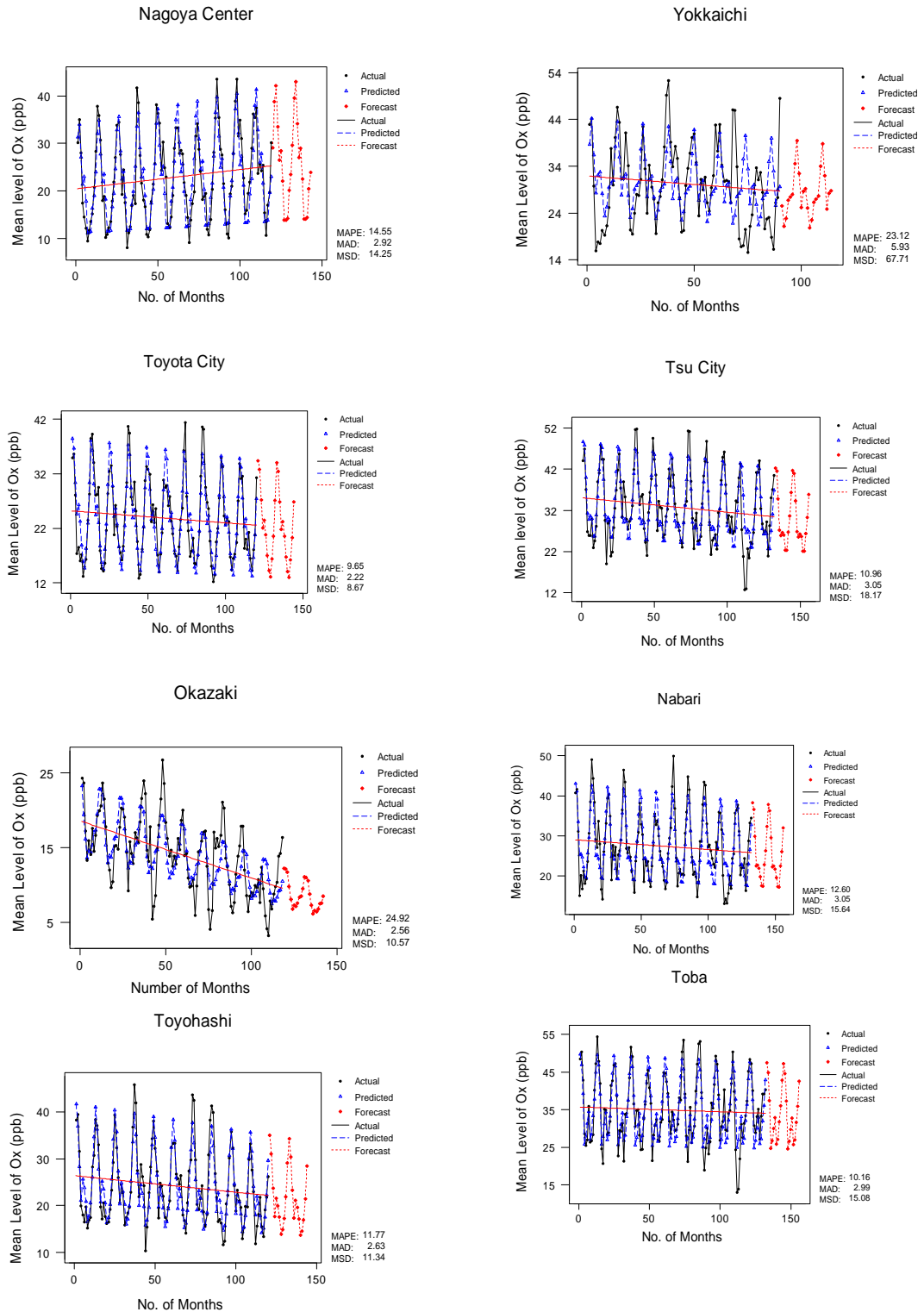Figure 2: Seasonally Adjusted Trend of the Monthly Mean Level of Ozone (O_x)

Amongst the selected sites, higher mean level of ozone and lowest mean level of NO, NO_2, NO_x, and NMHC existed at coastal resort site of Toba, while opposites were

found at the Okazaki (includes several national highway interchanges) where higher amount of precursor pollutants from traffic contributes to the added level of precursors. Red lines in the figure indicate the average trend of the monthly mean level of ozone. Table 1 shows the trend equations predicting the monthly mean levels of ozone and precursors at the selected sites.

Table 1: Trend Equations Predicting the Monthly Mean Levels of ozone and precursors

Sites	Trend Equations	Significance (MAPE) Value
Nagoya Center	O_x (ppb) = 20.55 + 0.0424*t; NMHC (ppb)= 356.80 – 1.50*t NO (ppb)= 14.67 – 0.022*t	O_x:34.96 NMHC:21.38 NO:87.52
Toyota City	O_x (ppb) = 25.23 - 0.022*t; NMHC (ppb)= 262.67 – 0.48*t NO (ppb)= 8.49 + 0.014*t	O_x:9.65 NMHC:11.75 NO:14.26
Okazaki	O_x (ppb) = 18.59 - 0.076*t; NMHC (ppb)= 392.29 – 1.30*t NO (ppb)= 122.15 – 0.066*t	O_x:24.92 NMHC:10.99 NO:12.28
Toyohashi	O_x (ppb) = 26.39 - 0.035*t; NMHC (ppb)= 206.74 – 0.48*t NO (ppb)= 9.59 + 0.013*t	O_x:11.77 NMHC:11.13 NO:14.29
Yokkaichi	O_x (ppb) = 31.92 - 0.036*t; NMHC (ppb)= 157.88 – 0.35*t NO (ppb)= 2.28 + 0.064*t	O_x:23.12 NMHC:15.49 NO:35.97
Tsu	O_x (ppb) = 35.07 - 0.035*t; NMHC (ppb)= 176.75 – 0.74*t NO (ppb)= 3.35 + 0.014*t	O_x:10.96 NMHC:20.13 NO:18.77
Nabari	O_x (ppb) = 29.08 - 0.025*t; NMHC (ppb)= 142.93 + 0.35*t NO (ppb)= 2.87 + 0.028*t	O_x:12.60 NMHC:12.59 NO:14.26
Toba	O_x (ppb) = 35.71 - 0.013*t; NMHC (ppb)= 129.97 – 0.068*t NO (ppb)= 2.23 + 0.047*t	O_x:10.16 NMHC:53.92 NO:10.16

As shown in the Table 1, except for Nagoya center, all other sites exhibits a slightly downward trend in the monthly mean level of ozone but despite decreasing trend of NO level at Nagoya Center, monthly mean of Ox is increasing. The monthly mean level of NO is in slightly increasing trend in all the sites except for Nagoya center and Okazaki site. Monthly mean level of NMHC is also is decreasing trend in all the sites except for Nabari considered due to additional contributions of NHMC from biogenic sources.

3.2   Diurnal Patterns of Ozone (O_x) and its Precursors

Figure 3.1 shows the typical patterns of diurnal variations of ozone and its precursors at the selected sites of different land habitats. A day time increase and night time decrease in ozone levels were observed at all the sites. A peak level of ozone also appeared at about the same time of the day (14:00-15.00 hr) at all sites implying that ozone peak level was reached due to local photochemical processes, and an ozone lean level was reached in the late morning due to scavenging of ozone

by freshly emitted NO during the morning traffic rush (06:00- 07:00 hr). Peak levels of NO were found between 09:00-10:00 hrs in the morning contributed mainly by the traffic rush hours. Distinct afternoon lean and evening peak levels of NO were found respectively at about 15:00-16:00 hr and 20:00-22:00 hrs respectively at all the sites. Morning peak levels of NO_2 and NMHC also reached simultaneously at about 09:00 hrs and proceeded to the peak level of NO by about one hour in all the sites but the evening peaks of NO_2 and NMHC reached at about 20:00 hrs at all the sites. However, comparatively higher mean level of NO, NO_2, and NMHC were observed at the sites of Aichi prefecture compared to the sites of Mie prefectures considered due to higher of traffic as well as industrial activities in the Aichi prefecture.
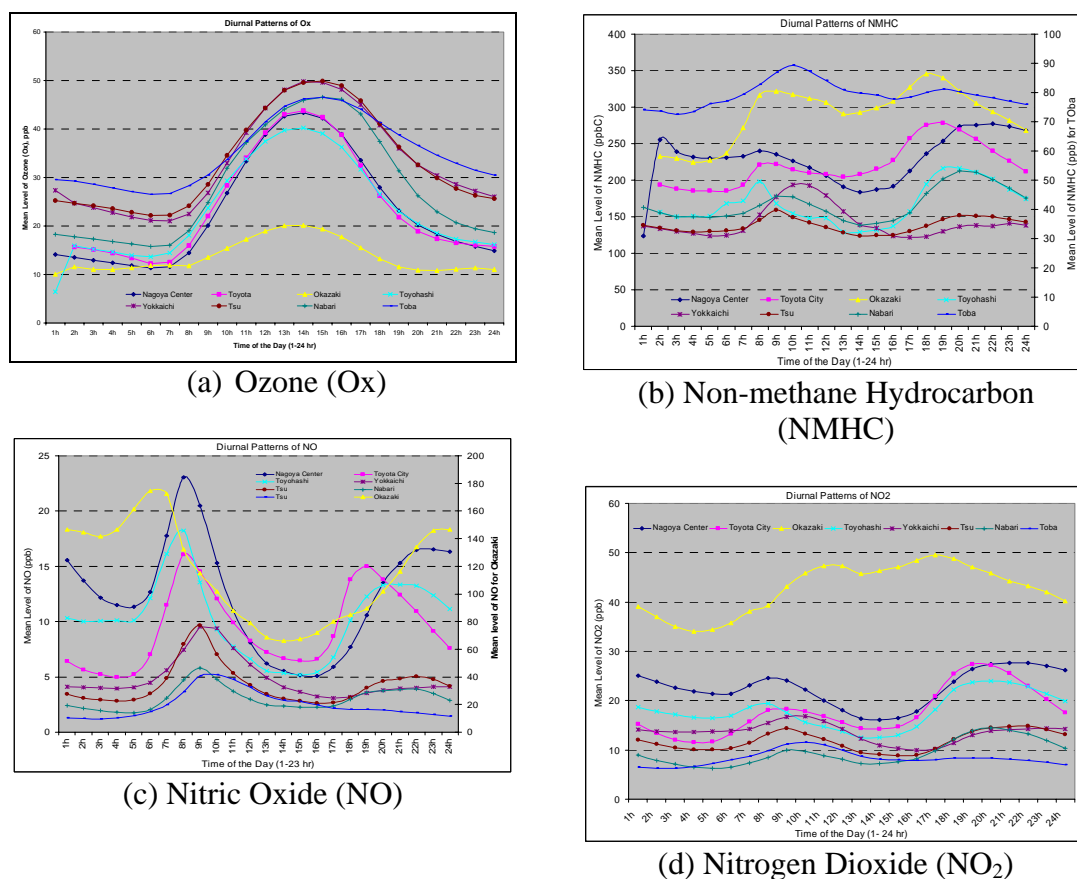

(a) Ozone (Ox)

(b) Non-methane Hydrocarbon (NMHC)

(c) Nitric Oxide (NO)

(d) Nitrogen Dioxide (NO_2)

Figure 3.1: Diurnal Patterns of Ozone (O_x)

Figure 3.2 shows the diurnal variations in the ratio of NO_2 and NO that follow a distinct pattern during the whole day and also showed a relationship with the variations in ozone levels. The ratio (NO_2/NO) reaches at the minimum level during the morning traffic rush when maximum level of NO emitted from the traffic and photochemical process begins. But the minimum levels reached first (about 08:00 hr) at the all the Aichi sites while the minimum levels reached at about 09:00 hrs at all the sites of Mie prefecture. However, the ratio starts increasing along with the consumption of NO_2 due to its photochemical conversion into O_x as well as simultaneously lesser amount of emissions of NO and NMHCs during the traffic

lean period (11:00 to 17:00 hr). As the ozone production level starts decreasing after the late afternoon, NO_2 level starts building up and the ratio reaches to the peak level at about 17:00-18:00 hr considered to be due to two reasons: (a) emission of NO from the evening traffic rush and other industrial and commercial sources; (b) emitted NO undergoes through the catalytic reaction process with the existing ozone to convert it again into NO_2 and O_2 molecule. However, the peak ratio starts decreasing again gradually during the night may be due to relatively less traffic emissions.

Figure 3.3 presents the diurnal patterns of the ratio NMHC/NOx for the selected sites. Similar to the ratio NO_2/NO, NMHC/NOx also follows a pattern of morning lean and afternoon peak level mainly attributed by the emissions patterns from traffic and industrial activities in the region but the magnitude of the ratio varies between the sites of the Aichi and Mie prefectures. This indicates that NMHC contributes in higher proportion in ozone productions processes at all the sites of Mie prefecture compare to the sites of Aichi prefecture.
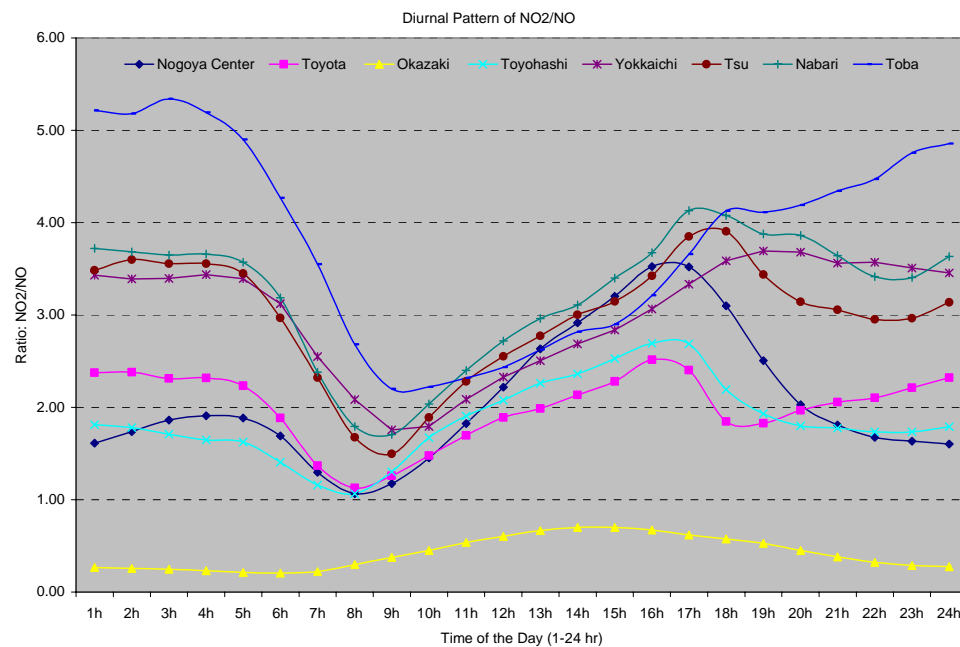

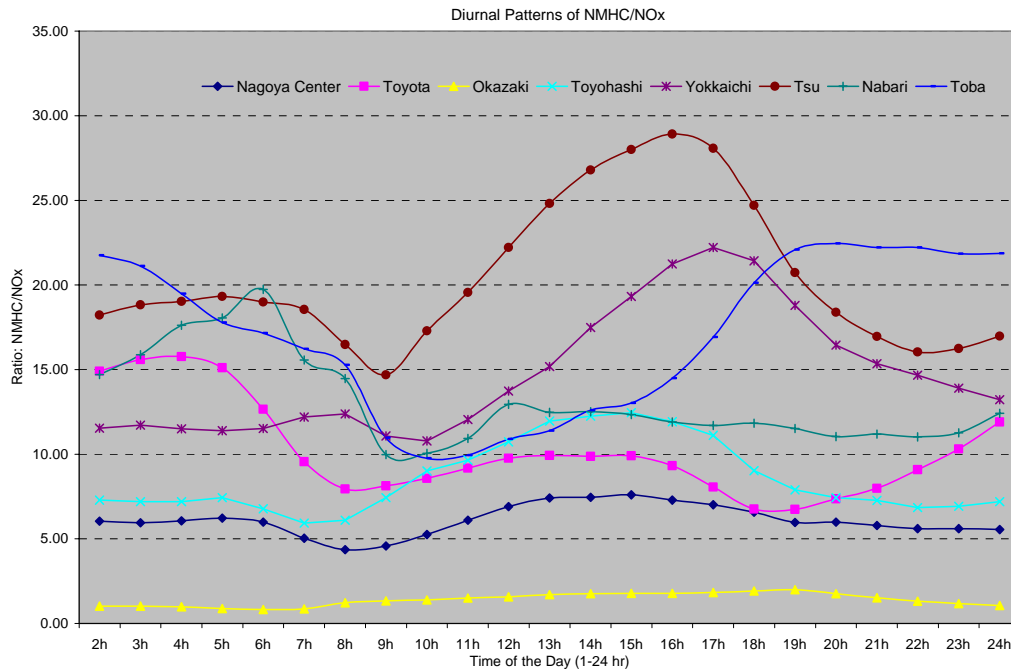Figure 3.2: Diurnal Patterns of NO_2/NO

Figure 3.3: Diurnal Pattern of NMHC/NOx at different Sites

Regarding the daily production and destruction of ozone at the selected sites, local ozone production rates (ranged from 1.39 to 4.54 ppb/hr) are relatively higher than that of ozone destruction rates (ranged from 1.39 to 3.10 ppb/hr). Despite highest rate of emissions of ozone precursors, at Okazaki, both production and destruction rate of ozone were the lowest perhaps due to wind transportation of the precursors to distance places before being converted into ozone. Opposites was the phenomena at Toba, where despite relatively lower level of precursor emission, higher level of ozone was observed as the precursors are transported from the urbanized cities by the north-west blown wind to this site.

3.3   Seasonal Variations of Ozone and Precursors

In general, stronger correlations exist between the parameters in the winter (December to February) compared to the summer (June to August) at all the sites although the degree of such relationships differs between the sites. Higher NO_2/NO ratios were observed at all the sites during the spring season and lower in the winter considered due to higher level of NO emissions from traffic and heating systems. Table 2 shows the mean of daily mean values of ozone, $NMHC/NO_x$, and NO_2/NO of different sites during different seasons (winter, spring, summer, and autumn). As shown in the Table 2, a higher mean level of ozone was observed during the spring season irrespective of the sites. Amongst the sites, higher mean levels of ozone were observed at the coastal cities of Yokkaichi, Tsu, and Toba.

Table 2: Mean of daily mean levels of O_3, NMHC/NO$_x$, and NO$_2$/NO

Sites	Parameters	Winter	Spring	Summer	Autumn
Nagoya Center	O_x (ppb)	16.17 ±8.01	32.88±11.60	25.77±12.85	16.11±10.10
	NMHC/NO$_x$	8.36±6.55	12.50±7.13	16.69±9.44	9.38±6.09
	NO$_2$/NO	2.62 ±3.08	6.82±11.81	6.24±11.79	3.45±4.46
Toyota	O_x (ppb)	17.99±6.62	33.35±10.12	25.39±11.94	18.49±8.83
	NMHC/NO$_x$	6.73±2.41	10.37±4.25	13.75±4.58	9.96±3.91
	NO$_2$/NO	2.04±0.96	3.70±1.14	3.14±1.11	2.57±1.17
Okazaki	O_x (ppb)	15.22±4.81	18.46±6.80	11.52±6.09	10.79±4.99
	NMHC/NO$_x$	2.17±1.40	2.19±118	2.53±1.28	2.23±1.09
	NO$_2$/NO	0.47±0.32	0.61±0.36	0.45±0.22	0.41±0.25
Toyohashi	O_x (ppb)	19.92±7.95	35.79±9.90	22.84±10.82	18.936±8.25
	NMHC/NO$_x$	5.33±3.12	7.81±4.56	10.20±4.75	8.0±5.04
	NO$_2$/NO	1.06±0.90	2.69±1.74	2.08±1.21	1.36±1.10
Yokkaichi	O_x (ppb)	26.56±10.66	39.45±13.31	29.39±14.19	24.57±12.23
	NMHC/NO$_x$	6.55±3.06	8.38±3.86	10.85±4.43	8.63±3.99
	NO$_2$/NO	4.27±4.87	5.31±4.39	5.46±5.26	4.92±6.72
Tsu	O_x (ppb)	29.50±10.20	43.26±12.09	30.67±13.66	27.25±10.09
	NMHC/NO$_x$	6.45±3.06	11.40±9.51	14.19±9.41	9.0±5.28
	NO$_2$/NO	3.38±1.54	4.42±1.49	4.30±3.07	3.86±2.93
Nabari	O_x (ppb)	24.36±8.99	38.55±10.02	25.35±11.84	21.17±8.47
	NMHC/NO$_x$	8.74±2.03	14.65±6.13	22.47±6.92	15.10±6.10
	NO$_2$/NO	3.21±1.12	4.60±1.60	4.19±1.69	3.86±1.55
Toba	O_x (ppb)	32.98±9.43	46.61±11.30	29.70±14.04	30.09±10.53
	NMHC/NO$_x$	7.28±4.57	11.71±10.18	15.79±15.04	9.52±7.67
	NO$_2$/NO	3.74±1.41	4.11±2.42	4.47±3.89	5.09±5.65

Despite higher level of NO emissions at the Nagoya center, and Okazaki, lower levels of ozone were observed at these sites indicating the scavenging of accumulated ozone by freshly emitted NO at the busy roads and several highway interchanges, and also wind transport of precursors to the distanced sites before being converted into ozone. A higher ratio of NMHC/NO$_x$ during the summer indicates higher contribution of NMHC from biogenic and anthropogenic sources in ozone production process.

3.4 Correlations Analysis of the Interaction Patterns between Ozone and its Precursors

Regarding the correlations between ozone and its precursors, the ratio of NO and NO$_2$ strongly influence the ozone production and destruction process but the strength of such correlations varies with the land habitats. Coastal resort site of Toba showed relatively higher correlations (R^2=0.73) followed by the other sites ($0.46 < R^2 = 0.64$). All the sites showed the linear relationships between NO$_2$ and NO. Significant correlations existed between NO$_2$ and NO in the range of ($0.40 < R^2 < 0.73$) which indicates that photochemical conditions (temperature, solar radiations etc.) are more or less similar in the whole region.

Highly significant correlations were found between NO$_x$ and NO ($R^2 > 0.91$) at Nagoya center, Toyota city, Okazaki, and Toyohashi sites of Aichi prefecture

indicating that NO emissions remains the dominant precursors to ozone at these sites. Strong relations were also found in other sites of Mie prefectures ($0.78 < R^2 < 0.87$) indicating that traffic and other industrial emissions remains the predominant sources of precursors albeit in a lower scale for ozone productions in the region. Moderate correlations also exist between NO_x and NMHC ($0.22 < R^2 < 0.46$) at all sites except for Toba where very weak correlations ($R^2 = 0.14$) exists. This reveals that contribution of NMHC on the ozone production is also higher in the more urbanized cities with characteristics of higher traffic density, industrial emissions sources, and higher number of gasoline stations compared to the less urbanized site of Toba with characteristics of relatively less traffic.

However, considering the slopes of the linear relationships between ozone and NO_2/NO as the intensity of the ozone production rates, Toyohashi, Toyota city, Okazaki, Nabari, and Tsu city sites showed the relatively higher intensity for ozone production (slope > 3.00) while for other sites showed relatively lower intensity and the slope values remain below 1.0. This indicates that influence of the ratio of NO_2 and NO on the ozone production is significantly higher at the more urbanized sites compared to the other sites. On the other hand, linear relationship between ozone and NMHC/NOx at all the sites showed very low slope values (<1.0) indicating insignificant influence of NMHC on the ozone production processes.

3.5 Seasonal Relationship in Interaction Pattern among Precursors
A stepwise multiple regression analysis between Ox and its precursors as well as meteorological parameters (wind direction, wind speed, and temperature) was done to examine the partial correlation coefficients of the parameters influencing the relationship. We considered partial correlations coefficients over 0.1 (10%) as significant parameters influencing the relationships with O_x. Table 3 shows the parameters that significantly influence the relationships for different seasons.

Significantly strong relationships between NO_x and NO existed at all sites with slight variations in different seasons ($R^2 > 0.60$) indicating that dominant sources of NO emissions remain same all over the year. Correlations between NO_2 and NO at all the sites showed a moderate relationships ($0.21 < R^2 < 0.48$) but varied with the land habitats. Regression results between ozone and NO_2/NO for different seasons have been presented in the Table 4.

Table 3: Parameters Influencing the Ozone Level (Partial Coefficients in Parentheses)

Sites	Winter	Spring	Summer	Autumn
Nagoya Center	NO (0.15), NMHC/NOx (0.43)	NO_2 (0.3), Temp (0.25), NO_2/NO (0.13), WS (0.11), NO (0.1)	NO_2/NO (0.19), NO (0.29), WS (0.23), NO_2 (0.18)	NO_2/NO (0.39), NO (0.15), WS (0.17), NMHC (0.13)
Toyota	NO_2/NO (0.31), NO(0.20), WS(0.20)	NO_2/NO (0.31), NO2(0.48)	NO_2/NO(0.67), NO_2 (0.28), CO(0.17)	NO_2/NO (0.59), NO_2 (0.14),
Okazaki	NO(0.55), WS (0.23), NMHC/NOx (0.15), NO_2/NO (0.14)	NO_2/NO (0.18), NO_2 (0.16), WS (0.34)	NO_2/NO (0.21), NO_2 (0.49), W S (0.18)	NMHC/NOx (0.19), NO(0.32), NO_2 (0.16), WS (0.23)
Toyohashi	NO_2/NO (0.44), WS (0.12), NO(0.14), NO_2 (0.13)	NO_2/NO(0.59), NO (0.29), NMHC/NOx (0.28)	NO2/NO (0.80), NO_2 (0.18), NO (0.14), NMHC (0.18), NMHC/NOx (0.18)	NO_2/NO (0.74), NO_2 (0.20), NO (0.27), NMHC/NOx (0.20), NMHC (0.16).
Yokkaichi	NO_2(0.44), NO (0.14), WS (0.11)	NO_2 (0.32), NO (0.18)	NO (0.28), NO_2/NO (0.15)	NO (0.27), NO_2 (0.18), NO_2/NO (0.16), WD (0.12)
Tsu	NO_2 (0.24), WS (0.15), NMHC (0.15)	NO_2(0.22), NO (0.19)	NO (0.51), NMHC (0.22)	NO (0.27), NMHC/NO_x (0.15), NO_2 (0.12)
Nabari	NO_2 (0.37), WS (0.29), NO_2/NO (0.24)	NO_2 (0.41), NO_2/NO (0.30), WS (0.28)	NO_2/NO (0.27), NO (0.23)	NO_2/NO (0.42), NO_2 (0.22), WS (0.16)
Toba	NO_2 (0.83)	NO_2 (0.23), NO (0.11)	NO(0.37), NO_2 (0.21), WD (0.17)	NO_2 (0.18), WD (0.14), NO (0.11)

Table 4: Relationship of NO_2/NO and NMHC/NO_x with O_x for Different Seasons (R^2 values)

Seasons	NO_2/NO		NMHC/NO_x	
	Winter	Summer	Winter	Summer
Nagoya Center	0.37	0.00	0.60	0.18
Toyota	0.56	0.48	0.26	0.09
Okazaki	0.02	0.07	0.00	0.00
Toyohashi	0.75	0.50	0.12	0.00
Yokkaichi	0.11	0.12	0.21	0.08
Tsu	0.34	0.11	0.25	0.13
Nabari	0.33	0.31	0.00	0.00
Toba	0.07	0.06	0.22	0.02

It was found that, except for Okazaki, Yokkaichi, and Toba, significant correlations ($0.30 < R^2 < 0.75$) existed between ozone and NO_2/NO in the winter at Nagoya center, Toyota, Toyohashi, Tsu, and Nabari. However, less seasonal variations were found

at Toyota, Toyohashi, Tsu, and Nabari. Both Okazaki city and Yokkaichi city acts as sources of ozone precursors as Yokkaichi city includes major industrial installations of the region and Okazaki city includes several interchanges of national highways that passes huge volumes of traffics everyday. Although Toba is a coastal resort city but it produces less ozone precursors but the effects of meteorological factors significantly influences on the variations of ozone as well as precursors levels. Regarding the interaction pattern between ozone and the ratio $NMHC/NO_x$, significant effects of $NMHC/NO_x$ on ozone production process were found at Nagoya city center, Yokkaichi, Toyota city, and Tsu in the winter season only. For all other seasons, no significant relationships were found for all the sites indicating that influence of NMHC in ozone production processes are less compared to NO_2/NO.

4. CONCLUSION

Characteristics of interaction pattern of ozone (O_x) and its precursors (NO, NO_2, NO_x, and NMHC) at eight different land habitat sites of Aichi and Mie prefectures showed some interesting relationship between ozone and the photochemical indicators (NO_2/NO, and $NMHC/NO_x$) in terms of the trend, diurnal variations, and seasonal effects at different sites. The ozone production and destruction processes are greatly influenced by the interactions between the precursors (e.g. $NO-NO_2$, $NMHC-NO_x$) and the strength of such interactions is dominant at most urbanized sites. In all the sites, ozone interaction behavior is significantly influenced by the variations in NO_2/NO ratio but strength of such interactions varies with seasons, and with respect to land habitats. The small range in the ratios of NO_2 and NO in all the sites (mean value of $NO_2/NO < 5.0$) and moderate slopes between ozone and NO_2/NO indicates the similar dominant sources of precursors (e.g. traffic emissions) and generally lower level of ozone. However, relatively higher daily production rates over destruction rates in ozone level also indicates the potential of gradual increase in the long term ozone level in the region.

ACKNOWLEDGEMENTS

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EFFECT OF THE VERTICAL RESOLUTION IN THE UPPER TROPOSPHERE AND LOWER STRATOSPHERE ON OZONE ABUNDANCE ACROSS THE TROPOPAUSE

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ABSTRACT

Stratospheric chemical transport model of Meteorological Research Institute (MJ98-CTM) is used to investigate the effects of model vertical resolution on the distribution of chemical species, particularly ozone across the tropopause. The dynamical module is a full primitive spectral model, which includes major physical processes. The chemical module treats 34 long-lived species including 7 families, and 15 short-lived species with 79 gas phase reactions, 34 photochemical reactions and 9 heterogeneous reactions on polar stratospheric clouds and sulfate aerosols.

Transport scheme is a flux form semi-Lagrangian type in the vertical and, at once, a simple semi-Lagrangian type in the horizontal with cubic interpolation. Model horizontal resolution is a T42 (2.8 degrees, 64x128 grids in latitude and longitude) truncation and the model top is fixed at 0.01 hPa (80 km). Control run was performed with 45 layers (T42L45), the vertical grid spacing of which is about 2km above the upper troposphere. Two experiments run are made by increasing the vertical resolution to 68 layers of 500 m thickness above 100 hPa or to 80 layers of 500 m above 300 hPa. The experiment runs are found to yields better ozone vertical profiles in the tropical lower stratosphere, indicating that the strength of the simulated Brewer-Dobson circulation was closely dependent on the accuracy of winds and vertical resolution in the tropical and mid-latitude lower stratosphere.

Key words: simulation, ozone, chemical transport model, upper troposphere and lower stratosphere

A STUDY OF PHOTOCHEMICAL POLLUTION IN İSTANBUL

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Hourly ozone and nitrogen oxide concentration levels measured between 2001-2004 in Kadıköy and Saraçhane – two urban districts in Anatolian and European sides of İstanbul, respectively – are analyzed. Concentration levels exceeding 100, 150, and 240 μgm^{-3} are selected in order to determine photochemical pollution episodes within the period. The highest ozone concentration was observed in Saraçhane on 10th of August 2001 as 310 μgm^{-3}. On 21st of June 2003, ozone concentration of 163 μgm^{-3} and on 21st of June 2003 in Saraçhane, ozone concentrations up to 225 μgm^{-3} were observed in Kadıköy. In 27th of August 2002 episode, ozone concentrations around 116 μgm^{-3} were detected in Kadıköy. It is found that high concentrations of photochemical smog are associated with relatively high pressure systems having very low wind speeds or calm conditions and sunny days with maximum temperatures above 25°C.

Key Words: Ozone, photochemical pollution, İstanbul, Pearson's correlation

1. INTRODUCTION

İstanbul is a city with a population of over 10 million people and located at 41°N and 29°E coordinates (Figure 1). Bosporus, a sea water strait extending from Black Sea to Marmara Sea, divides the city into European and Anatolian sides. The city has experienced a rapid growth in urbanization and industrialization. Statistics show that the population of the city is over 10 million and there are more than 2 million motor vehicles (Anonymous, 2000) contributing to the environmental problems of the area. Black Sea in the north and Marmara Sea in the south produce a differential heating of surfaces, leading to different meteorological conditions that may play a role in the transport of ozone. The complex terrain of İstanbul also influences the circulation systems over the city. The city experiences a transition climate between Mediterranean and temperate climate types. Strong inversion conditions in the summer period sometimes cause ozone concentrations to reach maximum levels in the late afternoon hours (Topçu *et al.*, 2002).

Ozone levels in Southern Europe and Mediterranean region have been studied by Klemm *et* al., 1998, Gusten *et al.,* 1997, Peleg *et* al., 1997. Kalabokas and Bartzis, 1998 studied the Aegean region. Photochemical pollution in İstanbul has also been studied by Anteplioğlu, 2000, Kocak *et* al., 2000, Topçu and İncecik, 2002, and Topçu *et* al., 2003. In our study, the collected meteorological and air – quality observations by National Weather Service and the İstanbul Greater Municipality, respectively, are analyzed. The diurnal variations of O_3, NO_x and VOCs are

investigated for selected episodes in two stations on both sides of İstanbul. The NO_x and VOC sensitivities to ozone formation during these days are analyzed by examining the correlations between ozone and its precursors.
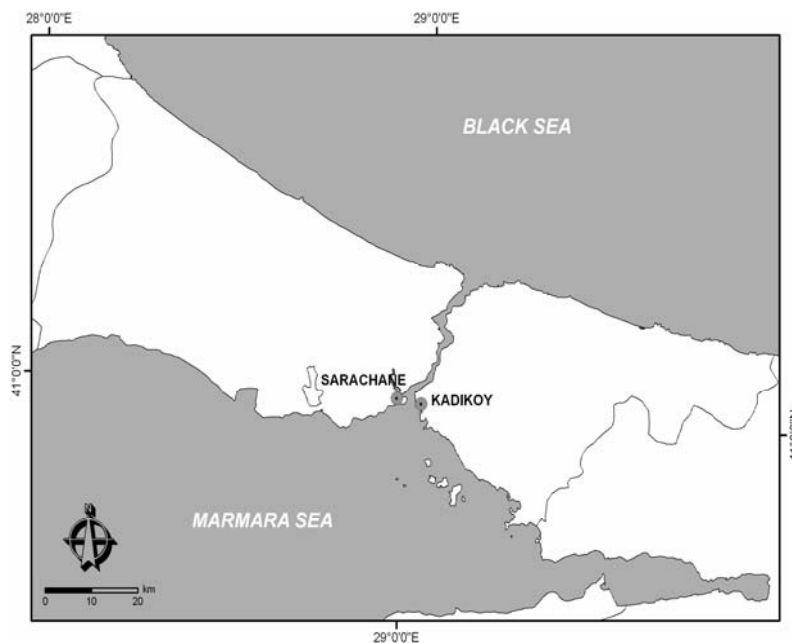

Figure 1. Map of the study region and locations of the air – quality stations

2. MATERIALS AND METHODS

2.1. Data and Statistical Analysis

Air quality data used in the study are obtained from İstanbul Greater Municipality between years 2001 to 2004. The selected stations for air quality data are the Kadıköy station on the Anatolian side and the Saraçhane station on the European side. Pollutants measured at the Kadıköy and Saraçhane stations are CO, NO, NO_2, NO_x, and O_3. Starting from 2002 in Saraçhane and 2003 in Kadıköy, Total Hydrocarbons (THC), Methane (CH_4) and non – Methane Hydrocarbons (nMHC) were added to the analyzed parameters. NO_x species are monitored using the Chemiluminescence method, CO by IR Adsorption method, O_3 by UV Photometry method and HC by Gas Chromatography (FID).

Statistical techniques are used for the quality control of the dataset. Days containing more than 12 hours of missing data and months containing more than 15 days of missing data are discarded from the dataset. Hourly ozone concentration levels exceeding 100,150 and 240 μgm^{-3} are selected in order to determine photochemical pollution episodes within the period. Based on the results of the statistical analyses, 4 episodes are selected for the study. These were 10th of August 2001 , 27th of August 2002 and 21st of June 2003 for the Kadıköy station and 21st of June 2003 for the Saraçhane station. Meteorological conditions during the episodes are presented in Table 1.

Table 1. Meteorological conditions during the episodes

Date	Mean wind speed (ms-1)	Wind direction	Mean Pressure (mb)	Max. Temp. (ºC)
10.08.2001	6.4	NE	1015	33
27.08.2002	4.5	NE	1018	26
21.06.2003	2.8	NE	1010	25

3. RESULTS

The highest ozone concentration recorded within the selected episodes are presented in Table 2. As seen in Figure 2, on 10th of August 2001, almost all concentrations are above 150 μgm^{-3}. The high concentrations are related to the high-pressure system over the region and the low wind speeds. We can see that peak concentrations are observed in the early morning hours pointing to a high accumulation rate of ozone over the region. The wind speed is at its minimum indicating a very restricted transport. The correlation factors of NO_2 and CO with O_3 are calculated as -0.39 and -0.23, respectively, meaning that NO_2 was more dominant over ozone formation than CO. These conditions can be explained as the result of high NO_x emissions or a possible advection of NO_x from other regions. As can be seen from Figure 3, NO_2 and CO are highly correlated with O_3 on 27th of August 2002 The destruction of ozone through reacting with NO, forming NO_2 can be clearly seen from Figure 3. The correlation factors are calculated as -0.94 and -0.85 for NO_2 and CO, respectively. The correlation coefficients show that both CO and NOx, with a higher NOx $-$ sensitivity, enhance the formation of ozone. Because of the high-pressure system and low wind speeds ozone was trapped over the region and the peak concentration was reached at nighttime. After the sunrise, with the increase in photolysis rate of NO_2 to NO, the ozone levels started to decrease. THC, CH_4 and nMHC datasets were also available for the period. Since nMHCs are the dominant organics in photochemical processes (Skov *et al.*, 1997), the relation between ozone and nMHCs is illustrated in Figure 3. There are positive correlations between all three hydrocarbon species and ozone. The correlation factors for THC, CH_4 and nMHC are calculated as 0.25, 0.19 and 0.25, respectively, agreeing that nMHCs are more important in ozone formation. These positive correlations show that with the increase in VOCs, ozone formation was slightly enhanced, especially by non $-$ methane hydrocarbons.

Table 2. Maximum concentration levels on the selected episodes

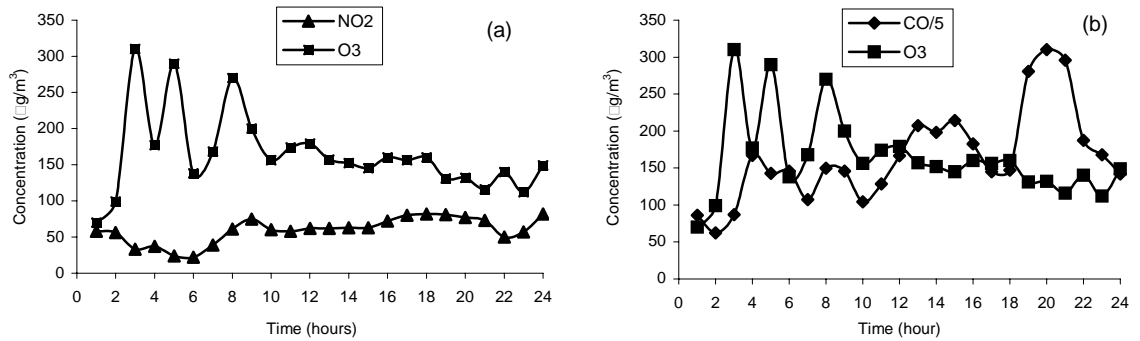| Episode date	Station	Maximum Concentration (μgm^{-3})
10.08.2001	Saraçhane	310
27.08.2002	Kadıköy	116
21.06.2003	Kadıköy	163
21.06.2003	Saraçhane	225

Figure 2. Diurnal variations of (a) O_3 and NO_2, (b) O_3 and CO (original values divided by 5) on 10th of August 2001

Diurnal variations of ozone, NO_2, CO and nMHCs in Kadıköy on 21st of June 2003 are presented in Figure 4. In Figure 5, relations between ozone and NO_2, CO and wind speed in Saraçhane on the same day are presented. As can be seen from the figures, there is a better correlation between the concentrations in Saraçhane. The correlation factors for NO_2 and ozone in Kadıköy and Saraçhane are calculated to be -0.54 and -0.63, respectively, showing that formation of ozone in Saraçhane was more enhanced by NO_x meaning that ozone formation in Saraçhane was more enhanced by CO. On the other hand, ozone formation in Kadıköy was NO_x – sensitive. The relation between VOCs and ozone are also analyzed for the Kadıköy region. The correlation factors are calculated as -0.44, -0.39 and -0.51 for THC, CH_4 and nMHC, respectively. Non – methane hydrocarbons were the dominant ozone formation initiators among the total VOCs. These correlation coefficients also confirm that ozone formation in Kadıköy was more NO_x – sensitive. The Pearson's correlation coefficient of wind speed with ozone in Kadıköy and Saraçhane stations are calculated to be 0.52 and 0.55, respectively.
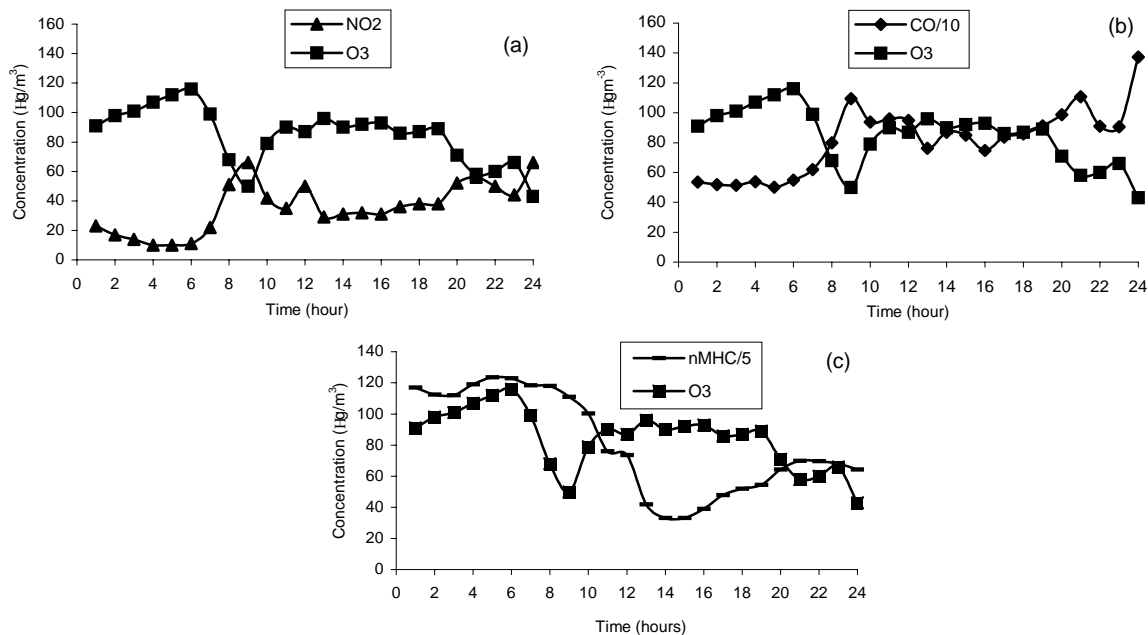
Figure 3. Diurnal variations of (a) O_3 and NO_2, (b) O_3 and CO (original values divided by 10) and (c) O_3 and nMHCs (original values divided by 5) on 27th of August 2002

Pearson's correlation factors for the selected episodes are presented in Table 3. Topçu and İncecik, 2002, reports that correlation coefficients calculated for the ozone months varied from 0.49 to 0.67 in years 1998 and 1999, which implies higher correlation than our calculations for 2001 to 2003. On the other hand, except for August 2001, Saraçhane episode, the selected episodes in this study presents very high correlations. The ozone production mechanism under intense solar radiation is also a key parameter and it is expected that high temperatures will enhance ozone production.

Table 3. Pearson's correlation coefficients between ozone, its precursors and wind speed for the selected days

	Pearson's correlation coefficients of Ozone			
	10.08.01 Sarachane	27.08.02 Kadikoy	21.06.03 Kadikoy	21.06.03 Sarachane
CO	-0.23	-0.85	-0.27	-0.75
NO	-0.16	-0.46	-0.47	-0.77
NO_2	-0.39	-0.94	-0.54	-0.63
NO_x	-0.31	-0.91	-0.56	-0.81
THC	-	0.25	-0.44	-
CH_4	-	0.19	-0.39	-
nMHC	-	0.25	-0.51	-
Wind	-0.39	-0.003	0.55	0.55
Temp.	0.14	0.74	0.74	0.08
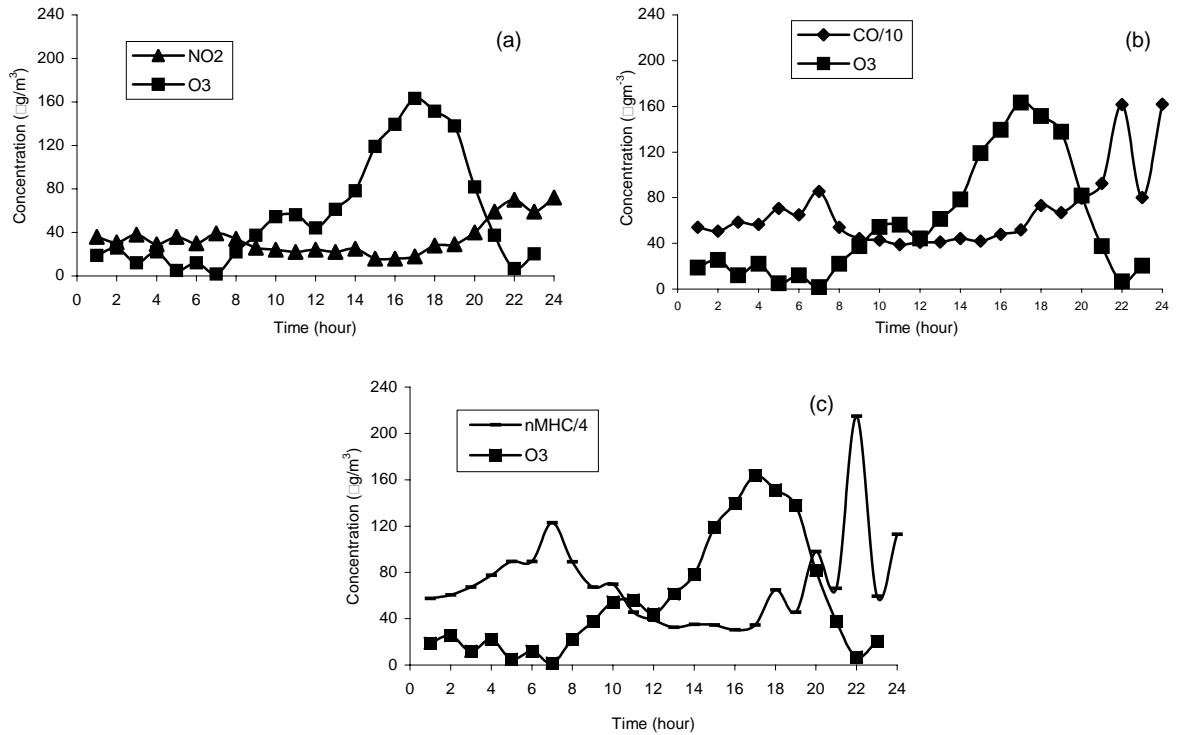
Figure 4. Diurnal variations of Ozone with (a) NO_2, (b) CO and (c) nMHCs in Kadıköy on 21st of June 2003

Figure 6 presents the correlation analysis between NO_x and NO levels from 2001 to 2003 in Kadıköy and Saraçhane, respectively. The results indicate very strong correlations to exist between the two precursors of ozone in both sites. NO plays the key role in formation of NO_x, and the high correlation coefficients between measured NO and NO_x values illustrated in Figure 6 confirms this relation.
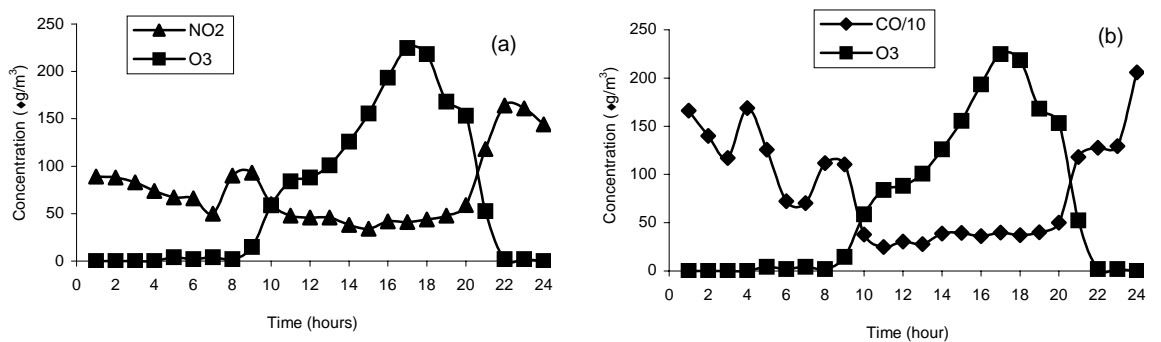

Figure 5. Diurnal variations of Ozone with (a) NO_2 and (b) CO in Saraçhane on 21st of June 2003
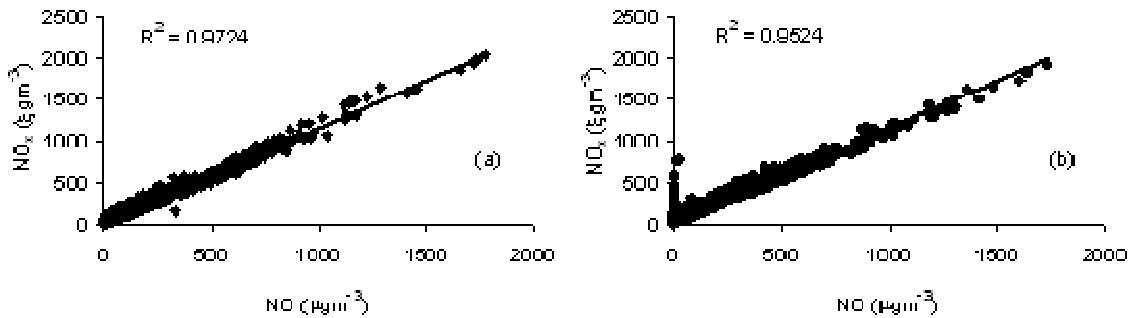
Figure 6. Relations between NO_x and NO levels in (a) Kadıköy and (b) Saraçhane

In order to estimate the transport to İstanbul on the episodic days, Hysplit model was run using the back – trajectory module. The results clearly show the north–easterly transport from the blacksea region to İstanbul city. Model results are presented in Figure 7.

4. CONCLUSIONS

İstanbul is experiencing a rapid and uncontrolled growth in urbanization, industrialization and transportation. Air quality data from the continuous measurements of ozone and its main precursors at two stations on both sides of İstanbul are analyzed in order to understand the relation between the various chemicals that are involved in photochemical processes in the atmosphere. The results show that high levels of ozone are observed mostly under anticyclonic conditions with relatively low wind speeds. It can also be concluded that Kadıköy experienced the higher ozone concentrations for the study periods. The correlations showed us that the ozone formation in İstanbul during these episodic periods was NO_x – sensitive. CO – involved mechanisms were also enhancing the ozone formation and NO_x species were dominant in Kadıköy whereas ozone formation was CO – sensitive in Saraçhane. Correlations between ozone and hydrocarbon species show that ozone formation by hydrocarbons was not as effective as NO_x species, with non – methane hydrocarbons dominating over other hydrocarbon species. The ozone trends on selected days imply that ozone was not local originated, but rather advective at early morning hours, except for 2003 episode. 2003 episode was probably local originated and illustrated a typical diurnal variation.

Ozone concentrations generally increased with increasing temperature, especially in Kadıköy 2002 and 2003 episodes, high correlations were determined between ozone levels and temperature. High ozone levels were also enhanced by light – wind conditions, as expected. Positive correlation between wind speeds and ozone levels were determined on June 2003 episode, meaning that wind speeds were not effective in dispersing the ozone accumulation and the production rate was dominant.
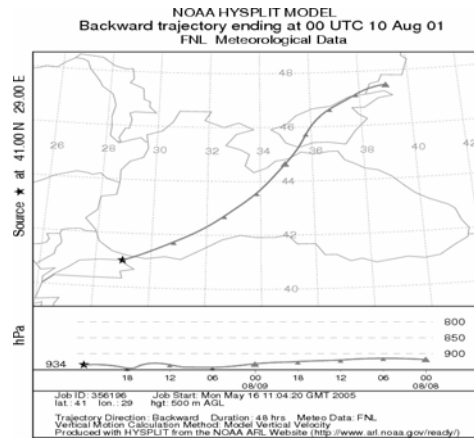
(a)
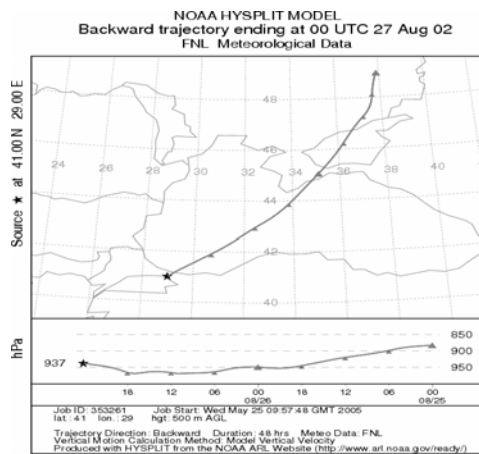
(b)
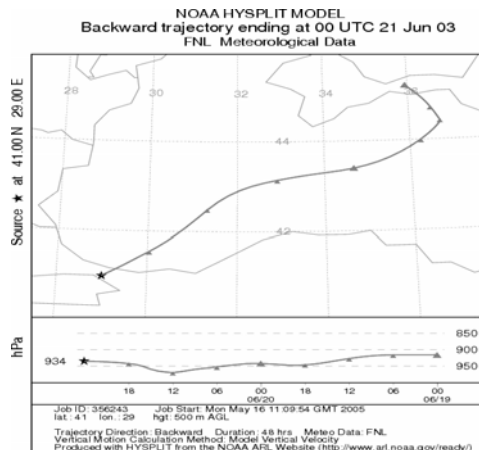
(c)

Figure 7. Hysplit results for (a) 10th of August 2001, (b) 27th of August 2002, and (c) 21st of June 2003

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VERTICAL STRUCTURE OF AIR POLLUTION LAYER IN POLAR INDUSTRIAL AREA

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ABSTRACT

The possibility of the using of surface ozone measurements for monitoring of atmospheric pollution is estimated. It is shown that the reactions of its species for ozone is quick for nitrogen oxide, and slow for carbon oxide in winter and spring conditions. The results of surface ozone measurements at levels 1.7 and 17 meters in the polar atmosphere are presented. It is found out the three types of surface ozone reaction for atmospheric pollution episodes. Directional analysis shows the connection of disturbance types with the industrial and transport objects. It is supposed that these types are bound up with the altitude of atmospheric pollution source.

Key Words: atmospheric pollution, surface ozone, nitrogen oxide, wind direction
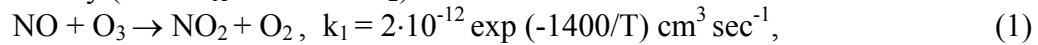
1. INTRODUCTION

The man-induced air pollution is always present in the modern industrial areas. Admixtures, while spreading away from sources, pollute the air around the industrial areas, changing its properties and resulting in negative effects on people's health, usually being toxic substances. The dynamics of polluting areas complex and depends much on the atmosphere condition, in the first place, on the velocities field of the atmospheric wind. Theoretical dynamics of air pollutions is studied on the basis of mathematical modeling of meteorological and chemical processes, taking place in the area of pollution (Bajin et al., 1991). When the description of a pollution near the source is used in a practical purpose, both models are used: the diffusion one for imponderable admixture (Fedosov, 1998), and the hydrodynamical model for admixtures heavier than atmospheric air (Shagapov and Galiaskarova, 2002). The theory does not answer many questions in specific meteorological conditions, in particular, the one concerning the atmospheric distribution of pollutions under a very weak wind, when admixtures are not carried away but are accumulated near, thus forming the observed structures of smog. For interpretation of the observations the altitude of the source of pollution is an important value, which tells upon its structure. For an experimental study of admixtures dynamics the chemical properties of substances, which make part of their composition, can be used. Besides, to find nitrogen oxides and carbon oxide the atmospheric ozone can be used, the quantity of which varies much under their influence. Thus, ozone observations on a regular basis can be applied for the atmosphere pollution monitoring. This approach is used in this

paper, which contains the results of experimental study of pollutions distribution at two altitudes under weak wind conditions.
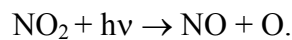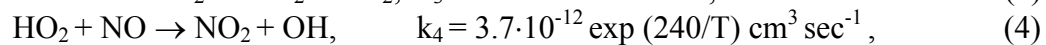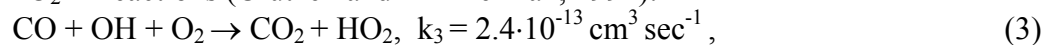
2. IMPACT OF ATMOSPHERIC POLLUTION ON OZONE

Variations of the surface ozone concentration (SOC) take place both at the chemical impact of the surrounding air and due to the transport of air masses with inhomogeneous chemical composition. The arising of SOC variations is possible as well during a long existence of ground inversion, when the SOC will be reduced because of deceased inflow of ozone from above.

The gas phase of air pollution is consisted of almost by half of nitrogen oxides NO_X and carbon oxide CO. These substances actively interact with surface ozone both directly (for $NO_X = NO + NO_2$):

$$NO + O_3 \rightarrow NO_2 + O_2, \quad k_1 = 2 \cdot 10^{-12} \exp(-1400/T) \text{ cm}^3 \text{ sec}^{-1}, \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O, \quad k_2 = 0 \div 10^{-2} \text{ sec}^{-1}, \qquad (2)$$
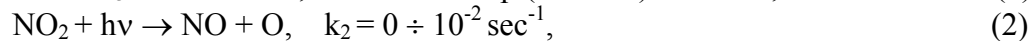
and forming in the case of CO an important precursor of ozone – hydroperoxide HO_2 in reactions (Crutzen and Zimmerman, 1991):

$$CO + OH + O_2 \rightarrow CO_2 + HO_2, \quad k_3 = 2.4 \cdot 10^{-13} \text{ cm}^3 \text{ sec}^{-1}, \qquad (3)$$

$$HO_2 + NO \rightarrow NO_2 + OH, \quad k_4 = 3.7 \cdot 10^{-12} \exp(240/T) \text{ cm}^3 \text{ sec}^{-1}, \qquad (4)$$

$$NO_2 + h\nu \rightarrow NO + O.$$

Here T is air temperature, the reaction with participation of quantum $h\nu$ designates photodissociation. The atomic oxygen, formed in the reaction (2), is quickly transformed into ozone. The range of values k_2 represents approximately the region of change of photodissociation rate in the high-latitude atmosphere (Beine et al., 1999). The characteristic time of photodissociation ranges from the value of 100 sec up to very large values depending on the ultraviolet radiation (UVR) intensity.

The characteristic time of nitrogen dioxide formation in reaction (1) will make $\tau_1(NO_2) = [NO_2]/k_1[NO][O_3] \approx 10^2$ s with $[NO_2] = [NO] = 10$ ppb, $[O_3] = 20$ ppb. With higher SOC the reaction time $\tau_1(NO_2)$ will still be less. Concentrations of ozone and nitrogen dioxide by means of reaction (1) will be changing quickly along with the nitrogen oxide concentration change in condition of weak photodissociation, when k_2 is little. The characteristics time of HO_2 formation in reaction (3) $\tau(HO_2) = [HO_2]/k_3[CO][OH] \approx 40$ s with $[OH] = 5 \cdot 10^5$ см$^{-3}$, $[HO_2] = 10^7$ см$^{-3}$, $[CO] = 150$ ppb; the characteristic time of nitrogen dioxide formation in reaction (4) will make $\tau_4(NO_2) = [NO_2]/k_4[NO][HO_2] \approx 10^4$ s. One can see, that the concentration of nitrogen dioxide will be changing much slower in reactions (3,4), compared to the reaction (1). The key moment here is the concentration of hydroxil OH which ensures the oxidation of CO. Formation of HO_2 from CO is weak at night when OH concentration is too little. But at daytime hydroperoxide HO_2 will be generated at considerable greater quantities and will weaken ozone decrease at reaction (1), interacting with NO. Thus carbon oxide CO will exert little influence on ozone decrease under NO increase at night, but this influence will become stronger at day and ozone decrease at reaction (1) will be smaller. These conclusions are correct under the conditions of weak photodissociation.

The influencing of reactions (1) – (4) on SOC is investigated quantitatively with application of the chemical model at work (Rumyantsev and Roldugin, 2003).
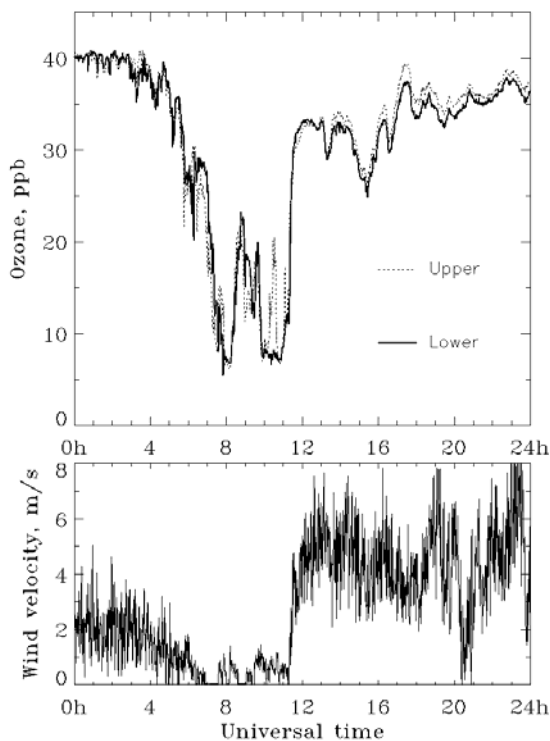
3. OBSERVATIONS AND RESULTS

The observations of SOC on two altitudes were curried out in December 2003 – April 2004 on the atmospheric station of Polar Geophysic Institute located in 1.5 km from the outskirts of Apatity town on the Kola Peninsula. Polluted air arrives to the station from the town and industrial area, which are situated on the east and north – east, and from the motorway, passed by not far (near 0.5 km) on the west, north and north – east. Long-range transport of air pollution from the industrial area of towns Monchegorsk and Olenegorsk, which are situated more than 45 km in the north – west, is possible also. There no industrial facilities or transport southwards of the station. The observational period corresponds to very weak and weak (in December – February), and moderate (in March – April) solar UVR in conditions of polar winter and spring.

Figure 1. Surface ozone concentrations at two levels (top) and wind velocity (bottom) on 19 December 2003.

SOC registration on two altitudes (1.7 and 17 m) is curried out by chemilumenescent ozonometers made in Polar Geophysical Institute. Nitrogen dioxide concentration is measured in period 29.01- 12.02.2004, on the site of location of the lower ozonometer, at the level 1.7 m. The temperature and humidity of air, atmospheric pressure on the ground level, velocity and direction of wind at altitude 10 m are determined by standard meteorological devices.

Characteristic feature of SOC behavior at the atmospheric station is appearance of ozone concentration disturbances, which represent ozone depressions which amount right up to 30 ppb and can last from one hour to tens hours. The disturbances contemporize with the stagnation periods often as it is shown by ozone measurements on one altitude (Beloglazov et al., 2002). Fast increases of nitrogen dioxide concentration take place simultaneously with ozone depressions as in (Beloglazov et al., 2002), being an evidence of chemical origin of ozone decreases. The observations on two levels show that the disturbance at the upper level does not ever accompany the disturbance at the bottom level. The change of SOC takes place under the decrease of wind velocity to small values, down to zero. The manifold of disturbances can divide to three types: 1) SOC behaviors in the lower and upper ozonometers are practically near in the disturbance period; 2) the disturbance takes place at the bottom but it is absent or is very weak at the top; 3) SOC behaviors have intermediate character when the disturbances at the top and bottom are practically
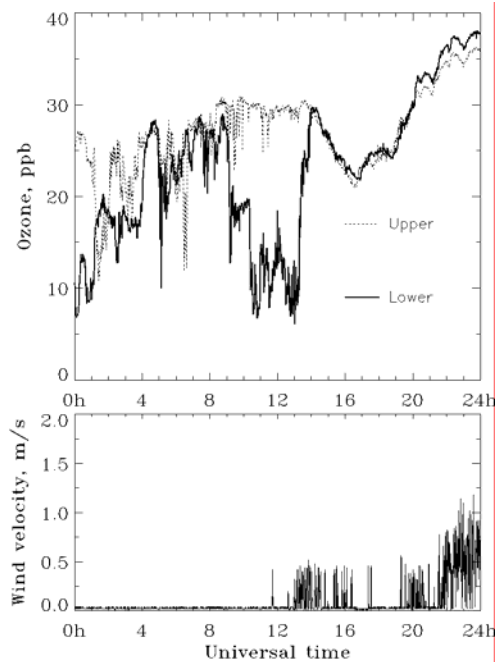
Figure2. As in Figure 1 for 3 January 2004.

near in a part of time but the disturbance at the top is weak during the rest of the time, or the disturbance at the top is distinctly less than the one at the bottom.

There were registered 118 events with duration from 1.5 to 20 hours for the observational period including 46 ones of first type, 23 of second type and 48 – of third type. Some of them are shown on Figures 1-3 in concordance with accepted classification. Figure 1 presents the case of December 19, 2003 when the event of type 1 happened about 0500-1130 UT. The ozonometer records are shown in the upper part of the Figure, the measurements results of the lower ozonometer are indicated with a thick solid line, and the results of the upper one are indicated with a thin point line. The results of wind velocity measurements are shown in lower part of the Figure. It is seen that the ozonometer records do not differ much for this disturbance; the disturbance occurs in the period, when wind velocity goes down to small values. The course of the disturbance of the second type is shown in Figure 2 for January 3, 2004. It is seen from Figure 2 that SOC at the lower level decreases to about 20 ppb at 0900-1400 UT, at the same time SOC changes weakly at the upper level. The SOC disturbance occurs in calm condition. The event of type 3 is analogously shown in Figure 3 for February 11, 2004. The deep bay to 30 ppb is observed at 1300 – 1400 UT at the lower ozonometer; this bay is recorded at the upper one only partially. The record of the upper ozonometer is nearing to the record of the lower one under small values of SOC. Wind velocity is insignificant and is less 1.5 $m·s^{-1}$ at this time.

4. DISCUSSION

Both meteorological and photochemical conditions exert some influence on the appearance of SOC disturbances. On the one hand, the meteorological factors determines the origin of areas with low values of the wind velocity, down to stagnation, in which atmospheric pollution is accumulated and ozone disappears; on the other hand, the appearance of SOC disturbances are determined also by the
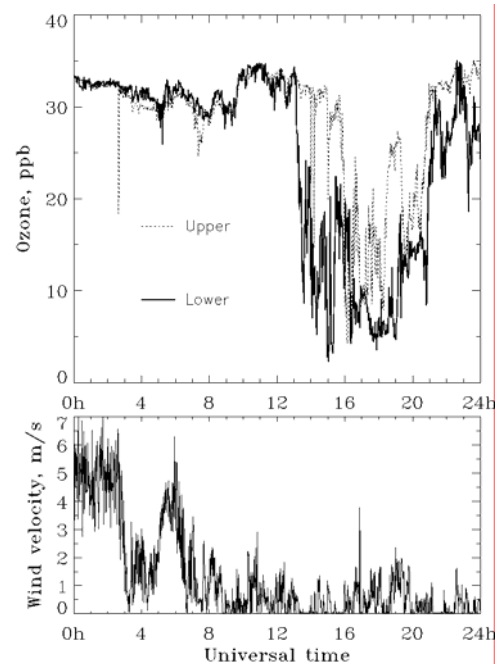

Figure 3. As in Fig. 1 for 11 February 2004.

photodissociation intensity preventing SOC from decrease. Monthly distributions of summary disturbance duration in local time are evidence of their gradual evolution from monotonic ones in December – January to ones with appearance of deep minimum near the noon in February; this minimum goes down to zero of duration in March – April. It demonstrates the growing importance of the photodissociation in formation of SOC disturbances.

For 81 events it is possible to determine the wind direction just before the disturbance and to find, which direction the air arrives from prior to the beginning. The distribution of different types of disturbances on wind directions befor the beginning of events is sh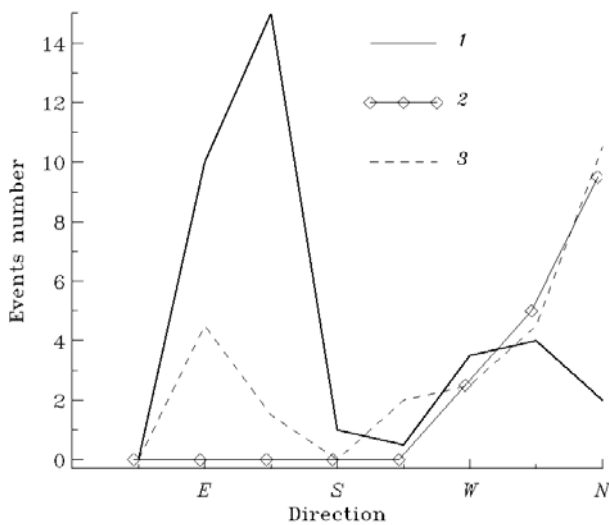own in Figure 4. Thick solid line represents the results for type 1, thin solid line marked by rhombus – for type 2 and dotted – for type 3. One can see that the disturbances of type 1 are connected mainly with the eastern wind, the disturbances of type 2 are absent at this wind, and the contribution of the disturbances of type 3 is not large at this wind. One could say that ozone disturbances in the air from the eastern sector take place only as registered at two levels (types 1 and 3).

Figure 4. Distributions of ozone disturbances on wind directions.

From the northwestern sector the air is brought in which both disturbances occur, the ones of types 1 and 3 and the ones, registered by the lower ozonometer only (type 2). The disturbances of types 1and 3 can be connected in this sector with three pointed sources i.e. Apatity town, motorway and towns of Monchegorsk and Olenegorsk.

It seems at the disturbances of type 2, the pollutions are registered, which arrive from motorway, located in the north, west and north – east. In this case the source of pollutions is situated near the ground surface. Pollutions have not time to rise up to 17 m level because of the small distance from the motorway to the registration site, and to have an effect upon ozone at this level. The thickening of pollutants near the ground is seen from NO_2 measurements, the results of which are given at (Pundt, 2003). In accordance with them the thickness of NO_2 layer makes up to 20 m leeward. It confirms the results of (Shagapov and Galiaskarova, 2002) about the smog height when his source is on the surface. Nitrogen oxide, incoming from the motorway in thin layer, affects the ozone at the lower ozonometer level only giving rise to ozone disturbance; nitrogen oxide is absent at the upper ozonometer level. In this case the disturbance of type 2 arises. It can explain nearly 20 % of all events. If the upper border of NO layer is cut and its altitude is changed, nitrogen oxide arrives to the upper ozonometer or does not arrive and the disturbance of type 3 arises. These disturbances can originate from the source, situated near the ground surface, under conditions that the altitude of the upper border of pollution layer is variable.

Then the upper ozonometer gets or does not get into the pollution layer. So nearly 40 % of all events can be explained. In these cases the pollution layer is thin and it is adjacent to the surface. The disturbances of type 1, representing about 40 % of the events, originate from either the high source or the remote source, pollution from which is spread along the vertical in the atmosphere.
Very few disturbances occur in air from south. They are related to types 1 and 3.

5. CONCLUSION

It is shown in principle the possibility of pollution monitoring in the industrial area as the results of surface ozone registration on the base of his interaction with nitrogen oxide and the results of the oxidation of carbon oxide. Ozone measurements at two altitudes (1.7 and 17 m) are curried out at the vicinity of a polar town during winter and spring 2003-2004. Measurements have shown the existence of three types of surface ozone reaction to atmospheric pollution. These three types are interpreted as the result of the chemical impact on ozone by pollution spreading on different altitudes. The pollution type has been chosen, which was thickening near the ground (lower 17 m). It is supposed that motor vehicles are one of sources this low – lying pollution. There are confirmed the conclusions of paper (Beloglazov et al., 2002) about the origins of SOC variations in conditions of weak wind basically.

6. ACKNOWLEGEMENT.

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REVIEW OF SURFACE OZONE AND ITS PRECURSORS IN URBAN ATMOSPHERE OF ISTANBUL, TURKEY FOR 2002-2003

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ABSTRACT

Surface ozone, the most well known substance within photochemical smog, plays an important role in affecting the regional climate and causing harmful effects on health and ecosystem. Surface ozone in urban areas is generated by a series of complicated photochemical reactions involving NO_x and HCs in the presence of sunlight. Surface ozone concentrations are increasing in the city depending on increasing number of cars that use mostly gasoline and poor dispersion conditions. Istanbul is one of the highly populated cities in the world and the most populated city in Turkey, with a population of about 12 million inhabitants. The history of photochemical air pollution in Istanbul is not long. The number of motor vehicles in Istanbul increased at a very fast rate (according to the figure of 2003 its about 1.7 million). It is two fold in the last ten years. High ozone days in ozone seasons are frequently observed when anticyclonic pressure systems are in the vicinity of Istanbul area.

In this study, the interaction patterns of nitric oxides and ozone are investigated based on measured data based in two urban sites in Istanbul, during the period of 1998-2003. The paper presents also an investigation of meteorological features that were present during high ozone days in Istanbul in the same period. The study identifies both synoptic and mesoscale controlling patterns as well as vorticity fields over the region and examines the relationships between surface ozone concentrations and meteorological parameters. In order to understand the characteristics of ozone formation in this region, meteorological parameters are examined according to classification of ozone levels and its precursors with high ozone and nonhigh ozone days. Furthermore the interactive characteristics between O_3 and NO_x are statistically studied.

Key Words: surface ozone, photochemical pollution, episode

1. INTRODUCTION

Surface ozone in urban areas is generated by a series of complicated photochemical reactions involving NO_x and HCs in the present o sunlight. Ozone the most well known substance within photochemical smog plays an important role in affecting the regional climate and causing harmful effects on health and ecosystem. Many studies of surface ozone problems in the lower surface atmosphere have been engaged in several countries (Hanna and Chang, 1995; Chang et al., 1998; Xu et al., 1998; Ghim et al., 2001). Photochemical smog problem is increasing in importance with the number of vehicles in the urban areas. Ozone episodes are rare in some of the cities which vehicle numbers are rather less than the developed countries. In China, ozone

episodes are rare because vehicle numbers are much less than those United States and other western countries (Xu et. al., 1998). As an example, Shanghai has a population of 10 million, but its vehicle number approximately of 300,000. Therefore, Chinese government has not paid a great deal of attention to the problem (Xu et. al., 1998). Furthermore, photochemical air pollution is a complex problem involving as it does both atmospheric diffusion processes as well as complex reactions. Photochemical O_3 problems become an especially important issue during the hot summers.

The history of photochemical air pollution in Istanbul is not long. The high O_3 levels now occur most frequently, O_3 pollution was low in 1998 throughout 2000 (Topcu and Incecik, 2002). The city did have serious SO_2 and TSP problems (Incecik, 1996; Unal et. al., 2000; Topcu et al., 2003). However, fuel use switched from high sulfur coal to liquefied natural gas in mid 1990s. In addition, the number of cars increased in Istanbul at a very fast rate, from 600,000 in 1990 to 1.7 million in 2003. As a consequence, air quality problems in Istanbul shifted from those caused by primary pollutants such as SO_2 and TSP to those caused by secondary pollutants such as O_3. Furthermore, O_3 problems will be not limited in Istanbul, quickly spread to many other cities. Surface ozone concentrations are increasing in the city depending on increasing number of cars that use mostly gasoline and poor dispersion conditions. Istanbul is one of the highly populated cities in the world and the most populated city in Turkey, with a population of about 12 million inhabitants. The number of motor vehicles in Istanbul increased at a very fast rate (according to 2003 Figureure it's about 1.7 million). It is two fold in the last ten years.

High ozone days in ozone seasons are frequently observed when anticyclonic pressure systems are in the vicinity of Istanbul area. Furthermore, photochemical O_3 problems become an especially important issue during the hot summers (Chang et al., 1998; Xu et al., 1998; Ghim et al., 2001)

In this study, the interaction patterns of nitric oxides and ozone are investigated based on measured data based in two urban sites in Istanbul, during the period of 2002-2003.

The paper presents also an investigation of meteorological features that were present during high ozone days in Istanbul. The study identifies the region and examines the relationships between surface ozone concentrations and meteorological parameters. In order to understand the characteristics of ozone formation in this region, meteorological parameters are examined according to classification of ozone levels and its precursors with high ozone and nonhigh ozone days. Furthermore the interactive characteristics between O_3 and NO_x are statistically studied.

2. INSTRUMENTATION AND MEASUREMENTS

Surface ozone concentrations have been measured in Istanbul in two sites, Kadikoy and Sarachane (Aksaray) in both Asian and European side of the city. An O_3 41 M ozone by Environment S.A. analyzer based on the absorption of UV radiation is

used. The NO_x analyzer, AC31M of Environment S.A is used. The system is based on the chemiluminescence's effect produced by the oxidation of NO by O_3. NO_2 is measured by converting it into NO using the thermal conversion method (GIM, 2000).

One of the best understandings of the indicators of ozone is its peak levels. The peak concentrations are considered in preparing of the air quality standards with their impacts on the health and ecosystem. Figures 1 and 2 give the time series of the daily maximum peak concentrations in 2002 and 2003. Kadikoy site indicates higher concentrations than those at Sarachane. This is due to the characteristics of the Kadikoy measurement station. This station is the center of the traffic in the area. However, Sarachane station expose to the ventilated area.

3. OZONE SEASON PROCESS AND EPISODES IN THE SUMMERS OF 2002-2003

Table 1 indicates the episodic characteristics in the city in 2003 two days before the episode, one day before the episode, episode day, and one day after episode and two days after episodes. Furthermore, ozone precursors were given for daylight hours with their peak levels for both sites in the city. In order to understand the ozone season process, ozone concentrations were classified according to 100 $\mu g/m^3$ as low and high ozone days. Table 2 shows the number of ozone days higher than 100 $\mu g/m^3$ in both sites for the summer months. Furthermore meteorological variables in episode period in 2003 is given in Table 3. June has much higher ozone days than the other months. This may be explained by the more intense solar radiation in June than the July and August (Figure 3).

Diurnal Variation
Photochemical ozone production takes place by photoxidation of CH_4, CO and NMHCs in the presence of sufficient amount of NO_x. In case of rich NO_x air, the production of NO_2 takes place by the reaction of NO and HO_2 or RO_2 which support the ozone production. However, in case of NO_x poor air, as like as rural atmosphere, these peroxy radicals react with ozone and lead to ozone loss (Lal et al,2000).

Average diurnal variations of ozone for June of the ozone seasons in 2002-2003 are shown in Figure 4. During the day, ozone concentration starts increasing gradually after sunrise, attains maximum value during noontime and then decreases. The daytime increase in ozone, which is a pronounced feature of an urban polluted site, is basically due to the photoxidation of the precursor gases such as CO, CH_4, and NMHCs.

In the diurnal cycle of ozone, the nighttime values are low, the minimum ozone concentrations are observed during early morning hours, near the sunrise. Low levels of ozone during early morning hours are due to the combined effects of chemical loss by NO and NO_2 species and suppressed of boundary layer mixing processes.

Diurnal variations in NO_x and NMHCs are shown in Figures 5 and 6 for the summer months in 2002-2003.

The average diurnal variations of NO_x, O_3 and NMHCs show buildup during morning and the late evening hours. The peak values of NMHCs indicate clearly traffic hours in both morning and evening in the city. It can be seen that the NO_x curve matches very well with the O_3 concentrations.

Ozone-NO_X Relationships
It is known that the number of ozone molecules that are produced for every NO_x that is oxidized. This process leads to negative correlation for the relationship between NO_x and ozone. Figures 7 and 8 show the O_3-NO_x relationships for 2002 and 2003 in the summer months.

Ozone and Wind Direction
In order to evaluate a relation between high and low ozone levels and wind direction, the frequency of occurrence of each wind sector and corresponding ozone mean were calculated for the summer months. Figure 9a shows that the wind direction is totally controlled by the orientation NE-ENE and 4% of calm winds for low ozone concentrations. However, dominant wind direction is SW-WSW with a 38.6% calms for high ozone days (Figure 9b).

4. CONCLUSIONS

Photochemical smog problem is increasing in importance with the number of vehicles in urban atmosphere of Istanbul. Furthermore, the variations of ozone in the lower atmosphere are greatly influenced by meteorological factors. In this study, the interaction patterns of nitric oxides and ozone were investigated based on measured data on two urban sites and meteorological factors in Istanbul, during the period of 2002-2003. The high ozone episodes characterized by southwest and west-southwest winds and calm conditions. There is a strong negative correlation between NO_x and ozone. The average diurnal variations of NO_x, O_3 and NMHCs support the process of the buildup during morning and the late evening hours. The peak values of NMHCs come from city traffic in both morning and evening in the city.

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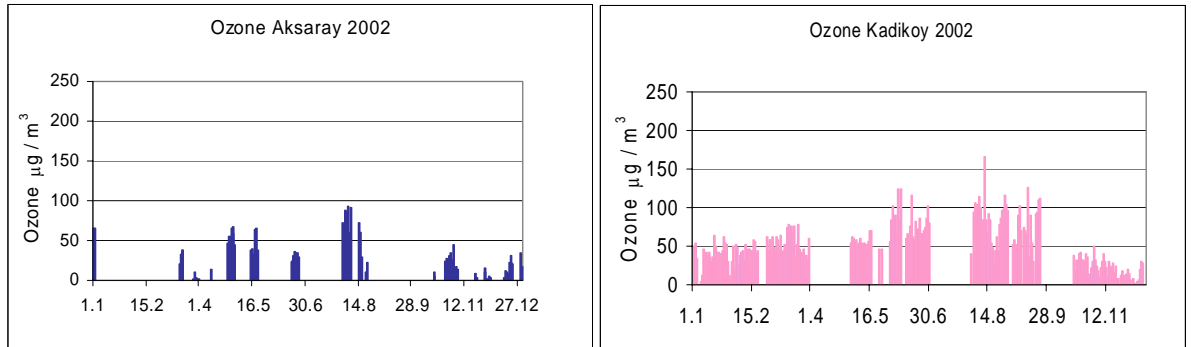
Figure 1. Daily maximum ozone concentrations in 2002 at Aksaray and Kadikoy.
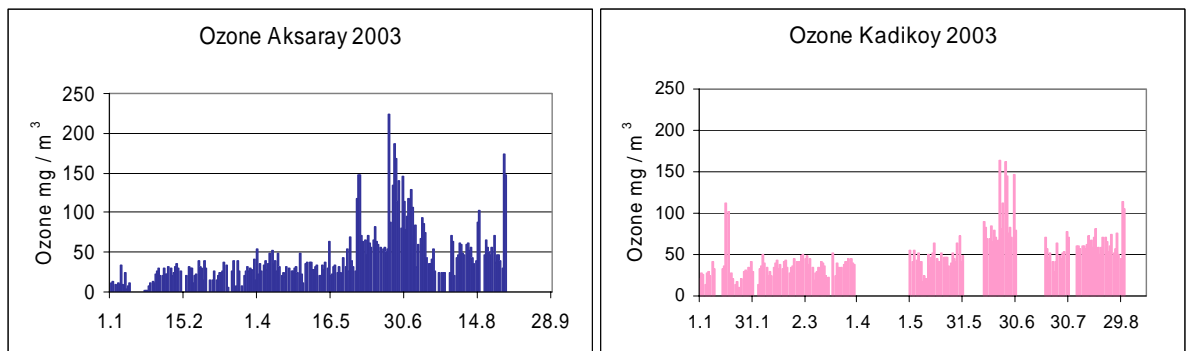
Figure 2. Daily maximum ozone concentrations in 2003 at Aksaray and Kadikoy.
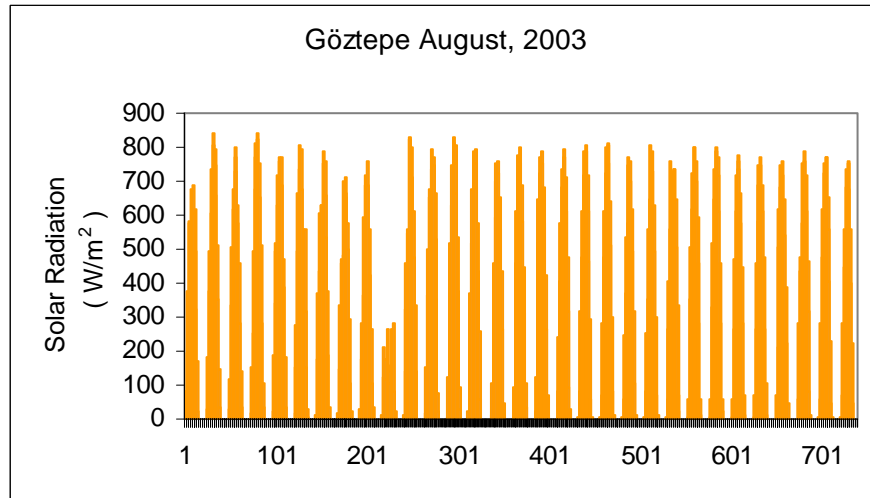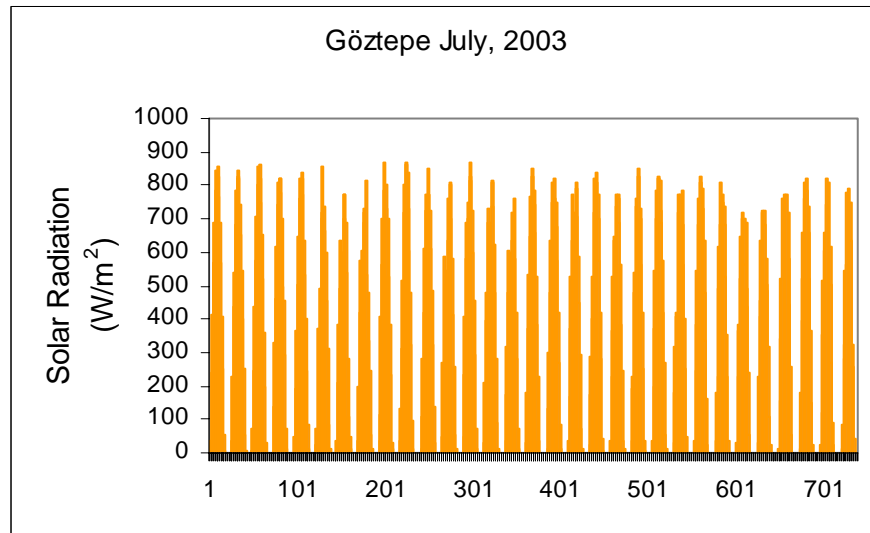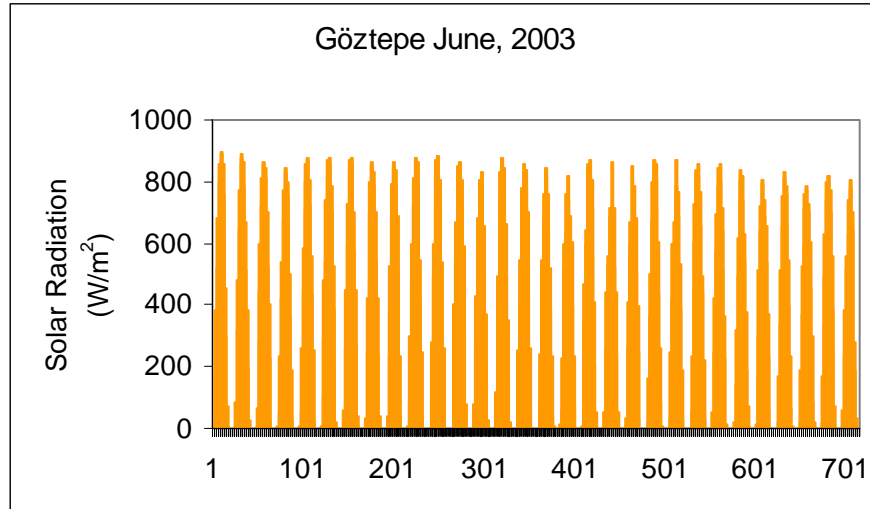
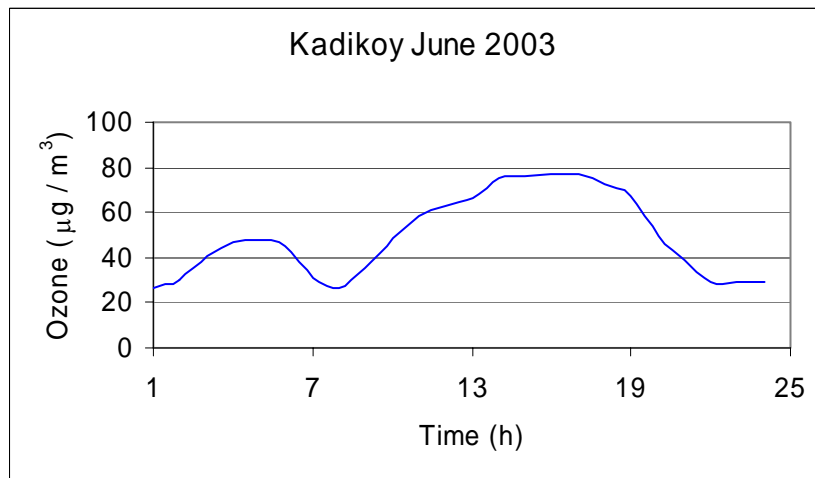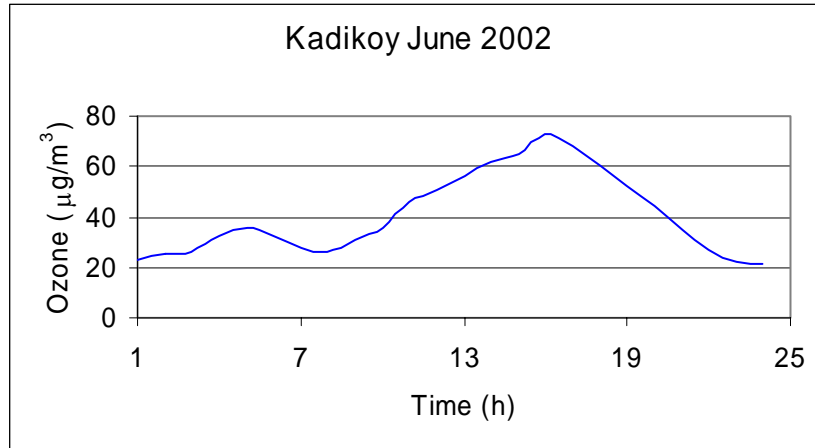Figure 3. Solar radiation in the summer months of 2003

Figure 4. Diurnal Variation of ozone in June of 2002-2003
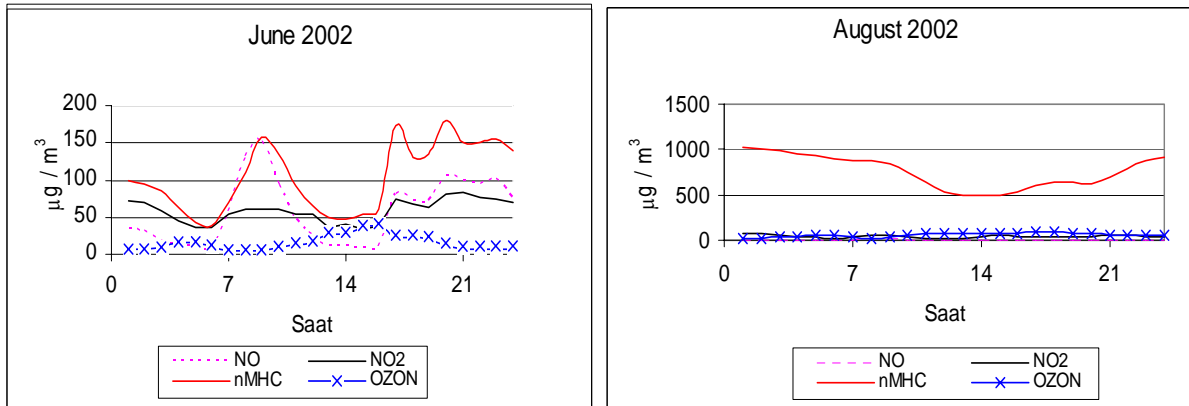
Figure 5. Diurnal variations of NO_x and NMHCs in 2002 summer months at Kadikoy (July 2002 data is not available)
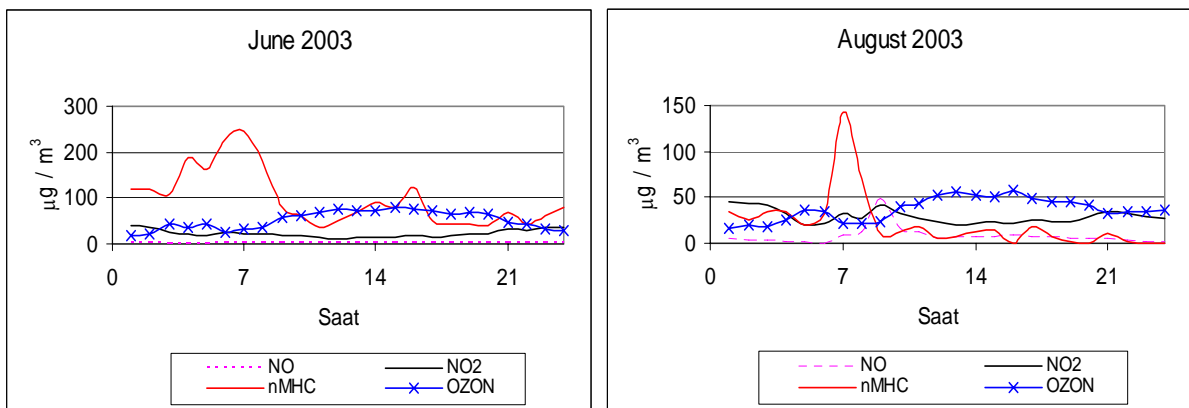

Figure 6. Diurnal variations of NO_x and NMHCs in 2003 summer months at Kadikoy (July 2003 data is not available)
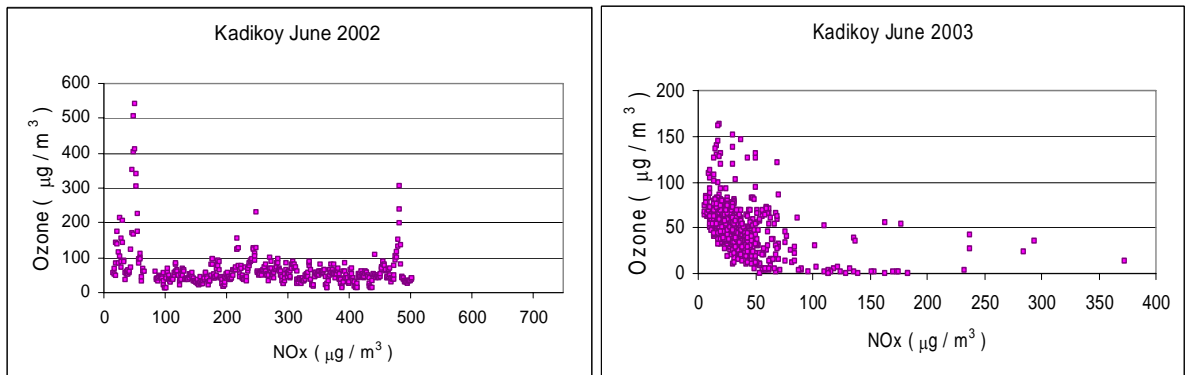
Figure 7. O3-NOx Relationships for June 2002 (r=-0.01) and 2003 (r= - 0.44)
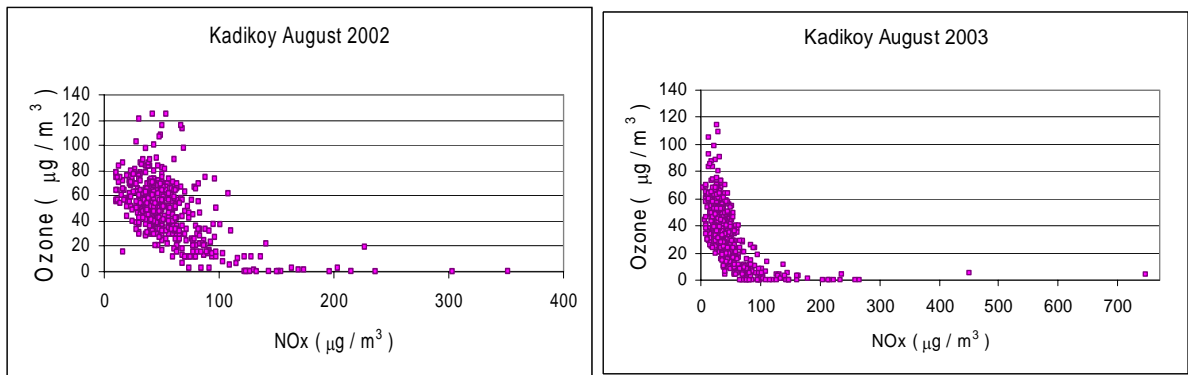

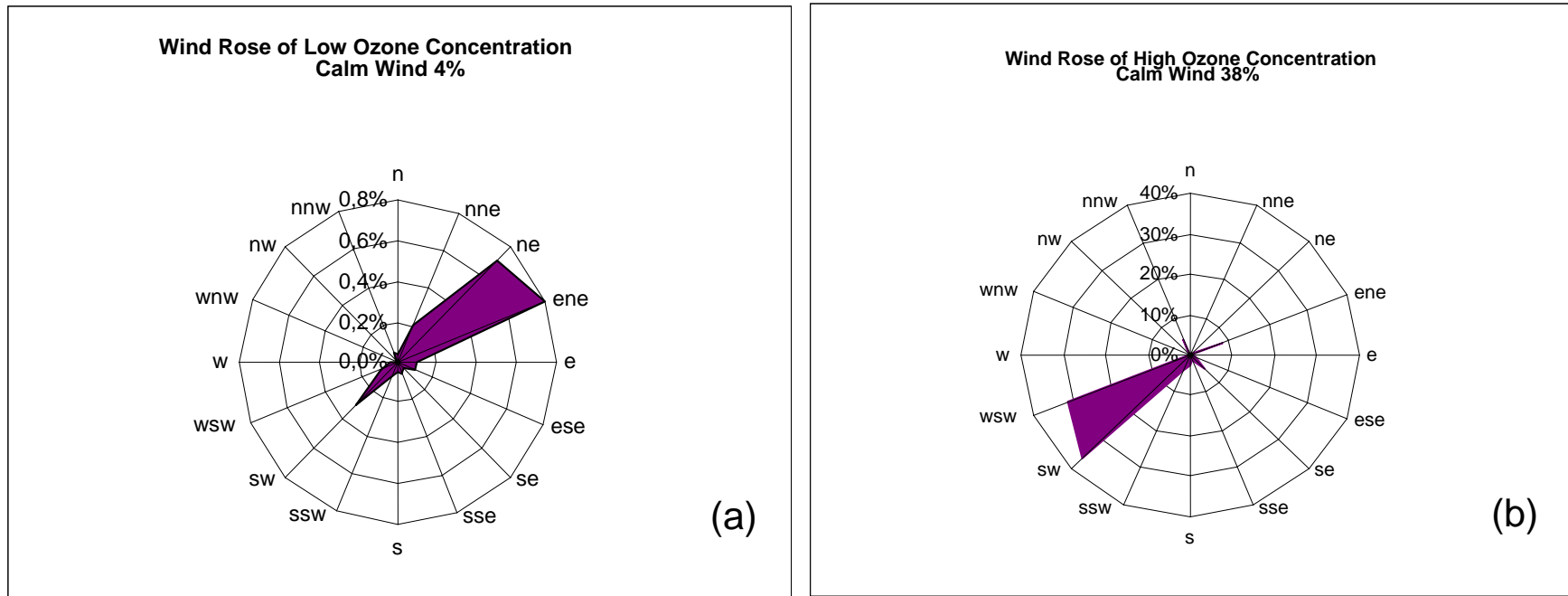Figure 8. O3-NOx Relationships for August 2002 (r=-0.55) and 2003 (r=-0.46)

Figure 9. Ozone pollution roses for summer months (June, July and August) in 2003 for (a) $O_3 < 100 \ \mu g \ / \ m^3$ and (b) $O_3 > 100 \ \mu g \ / \ m^3$

DECOMPOSITION OF GAS-PHASE OZONE USING NATURAL MANGANESE ORE AS A CATALYST AT ROOM TEMPERATURE

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ABSTRACT

This paper examines the catalytic decomposition of gas-phase ozone over natural manganese ore (NMO) as a catalyst at room temperature. It is known that NMO mainly consists of γMnO_2, which plays an important role in decomposition of ozone. For the practical application of ozone removal processes, an investigation was conducted for the pretreatment influence of catalyst on decomposition of ozone, especially calcination temperature. NMO was compared with pure MnO_2 and $MnO_2/\gamma\text{-}Al_2O_3$ as reference catalysts. It is found that the optimum calcination temperature is 400 C since MnO_2 is converted to Mn_2O_3 above 500 . For space velocity below 25,000 hr^{-1}, NMO and pure MnO_2 are known to have the same activities, and their conversions of ozone decomposition, and are higher than that of $MnO_2/\gamma\text{-}Al_2O_3$. The temperature-programmed reduction (TPR) experiments show that NMO has lattice oxygen as many as MnO_2 and more than $MnO_2/\gamma\text{-}Al_2O_3$ on initial temperature of reduction. Also the long-term test confirms that NMO is completely performed in redox cycle.

Key Words: Decomposition of ozone; Catalytic oxidation; Natural manganese ore (NMO); Manganese oxides

1. INTRODUCTION

Gaseous ozone is a chemical compound that has gained a lot of attention in the past years. The ozone layer in the stratosphere is formed through the solar radiation on molecular oxygen, and it protects biological organisms from harmful ultra-violet radiation (Cotton and Wilkinson, 1998). However, ozone in the troposphere is emitted from copiers, printers and water purification system, and is responsible for nausea, headaches and other respiratory illness especially in work environments (Naydenov and Mehandjiev, 1993). Also it enhances photochemical smog formed from reactions between VOCs and nitrogen oxides (Yamashita and Vannice, 1996). Because of its toxicity, the Occupational Safety and Health Administration has declared a permissible exposure limit of 0.1 ppm ozone for a period of eight hours at ground level (Nebel, 1978).

The technology of ozone decomposition is utilized in a number of applications. In airplane cabins, exterior air must be purged of ozone before it can be circulated (Dhandapani and Oyama, 1997). In office environments, cooling air from photocopiers and laser printers carries large amounts of ozone generated by corona discharge processes, and it must be treated before being released, and exhausted gas from deodorization and waste water systems must have its ozone levels reduced (Kent and Fein, 1987; tatsushima and Sakura, 1989).

Most of the works on gas-phase ozone decomposition are catalytically designed to destroy ozone in the air. The active components of the catalysts are noble metals such as Pt, Pd, Rh, etc. (Carr and Junction, 1982; Galligan and Dettling, 1995). But high price of the noble metal has encouraged the use of transition metals such as Mn, Co, Cu, Fe, Ni and Ag (Dhandapani and Oyama, 1997). Catalyst supports used are γ-Al_2O_3, SiO_2, TiO_2, zeolites and activated carbon (Heisig et al., 1997). Supported manganese oxides among oxides used in ozone decomposition have been identified as active oxide (Li et al., 1998; Radhakrishnan et al., 2001). Thus supported manganese oxides are known to be interesting catalysts because they have various types of labile oxygen that are necessary to complete a catalytic cycle. It is for this reason that supported manganese oxides have been used for catalyzing several chemical reactions including the reduction of nitric oxide, oxidation of CO, NH_3, methanol and ethanol (Kanungo, 1979; Stobbe et al., 1999).

In this paper, we report studies of the performance of NMO in ozone decomposition. NMO is composed of various metal oxides, mainly manganese oxides, and has the potential to be used as a catalyst for ozone decomposition. Furthermore, it is low-priced and is prepared by simply methods. The purpose of this paper is to examine the potentiality of NMO as ozone decomposition catalyst.

2. EXPERIMENTAL

The catalyst used in this study is NMO, which is mined in Australia. The NMO is crushed by a jaw crusher and ball mill and then separated to a mean particle diameter of 3 . MnO_2 and MnO_2/γ-Al_2O_3 are used for the activity of ozone decomposition and as the references for TPR. MnO_2 is a commercial product (Merck Co., Rahway, NJ), and MnO_2/γ-Al_2O_3 is prepared by the impregnation method. Impregnated catalysts are dried at 100 overnight. The dried material is then placed in a crucible for calcination. The material is heated to 400 C, calcined for 4 hr in air. Mn content of the $MnO_2/$ -Al_2O_3 is 2 wt.%. Also, NMO is calcined at 400, 500, 600 and 700 C for 4 hr in air respectively, to prepare the catalysts with different calcination temperatures.

The honeycomb catalysts are prepared by wash-coating catalyst powders made by previous processes with silica binder on the cordierite honeycomb (Corning Co., 200 CPSI) with square-shaped cells. The wash-coated honeycomb is blown with compressed air to remove excess slurry on the cordierite off and then is dried at 100 C overnight. These procedures are repeated to increase the amount of catalyst wash-coated on the surface of cordierite, and the honeycomb was calcined at 400 C for 4 hr in air. The active material weight was defined as the weight of all binding materials in each system. The weight of the cordierite is taken before and after impregnation, and the active material weight is 330 g /ℓ.

A schematic of the reactor unit used to test the catalyst activity is given in Fig. 1.
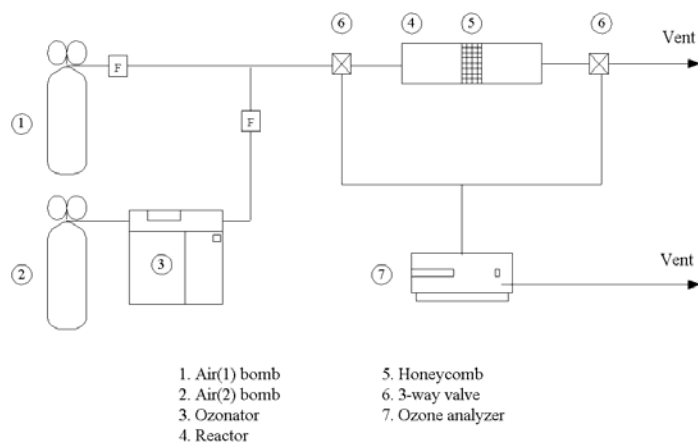
Figure 1. Schematic representation of the experimental apparatus.

A balanced air and air through an ozone generator (OZ BIO Co., Ltd) are used to maintain constant ozone concentration and space velocity. The gas mixture is passed through the honeycomb catalyst, and then vented. Flow rate is controlled by MFC (Mass Flow Controller, Model FC-280S, Tylan). Thermocouples and a pressure transmitter (Dwyer Instrument, Inc., Model 632S-1-LCD) are used to monitor the temperature and pressure drop. Standard conditions are operating temperature of 28 C, the range of linear velocity at the catalyst of 0 ~ 0.4 m/s, inlet ozone concentration of 1.0 ppm, a relative humidity of 60 % and the range of total flow rate of 0 ~ 20,000 cm^3(NTP)/s, corresponding to a space velocity of 0 ~ 68,000 hr^{-1}.

The ozone concentrations at the reactor inlet and outlet are measured using an UV photometric ozone analyzer (Thermo Environmental Instruments Inc. 49C O_3 analyzer) with a sensitivity of 0.001 ppm. The activity is evaluated isothermally at a given condition for at least 10 hr to ensure constant activity and steady-state conditions. Consecutive runs with new samples yield similar results, indicating the reproducibility of the experiments.

Temperature-programmed experiments are performed in a conventional TPR flow apparatus. Samples of 50 mg are heated from room temperature to 900 C in a mixture of 60 vol.% H_2 in Ar (50 ml min^{-1}), with a heating rate of 10 C/min. A cold trap is used for the removal of water. The apparatus is equipped with a thermal conductivity detector (TCD) to determine the hydrogen consumption during the

reduction. The concentration of hydrogen is measured by a gas chromatograph (Model HP 6890, Hewlett-Packard). Calibration of the TCD is performed by the injection of known amounts of Ar in the H_2/Ar flow, thus simulating H_2 consumption.

3. RESULTS AND DISCUSSION

The chemical and physical properties of the catalysts used in this study are summarized in Table 1. NMO exists in various forms such as pyrolusite, psilomelane, manganite, braunite and hausmannite in the natural state (Baller et al., 1976). From X-ray photoelectron spectroscopy (XPS) and chemical analysis, the NMO used in this study is found to contain manganese oxides as the main component and Fe_xO_y, CaO, MgO, SiO_2, and Al_2O_3. In more detail, most of the manganese oxide is in the form of β-MnO_2 (pyrolusite). $CaMnSi_4O_{18}$, KMn_8O_{16} (Cryptomelane) and $BaMn_8O_{16}$ (Hollandite) which are formed by the insertion of metal ion into manganese oxides, are present in small quantities. The structure of $\tilde{\ }MnO_2$ is tetragonal.

Table 1. Chemical properties of NMO (balance oxygen of Mn and Fe: 36.33 wt.%)

Compositions	Mn	SiO_2	Al_2O_3	Fe	CaO	MgO
Wt. %	51.85	3.13	2.51	3.86	0.11	0.25

In order to use NMO as ozone decomposition catalyst, effective calcination conditions must be made as a selection. Fig. 2 is the conversion of ozone decomposition with the space velocity as a function of calcination temperature. The conversion of ozone decomposition can be calculated based on a following formula;

$$\text{Conversion of } O_3 \text{ decomposition (\%)} = \frac{([O_3]_{in} - [O_3]_{out})}{[O_3]_{in}} \times 100 \qquad (1)$$

NMO catalyst calcined at 400 C shows the highest conversion. The dried NMO catalyst has less activity than NMO catalyst calcined at 400 C.
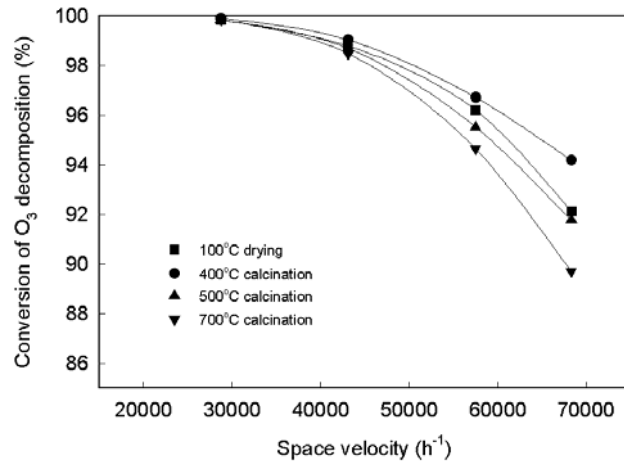
Figure 2. The conversion of ozone decomposition as a function of space velocity for NMO catalysts prepared at different calcination temperatures.

Kanungo (1979) is found that MnO_2 release the physically adsorbed water below 200 C, and chemically adsorbed water and surface hydroxyls are removed beyond 400 C. This result supports that the dried NMO catalysts could remove only the physically adsorbed moisture and the residual hydrated water may deteriorate the catalytic activity. The NMO catalysts calcined over 600 C are transphased by the release of lattice oxygen. According to Li et al. (1998), ozone adsorbs dissociatively on the manganese oxide catalyst to form an oxygen molecule and an atomic oxygen species. The atomic species react with another gaseous ozone to form a peroxide species and a gas-phase oxygen molecule and then the adsorb peroxide species decomposed to form a gas-phase oxygen molecule (Li et al., 1998). Consequently, the mechanism of ozone decomposition must consist of redox mechanism. In the viewpoint of manganese oxidation state, Mn_2O_3 may have less the capacity of redox function than MnO_2.

To inquire into the effect of calcinations temperature on NMO catalyst, the analyses of XRD and BET are investigated. In Fig. 3, the XRD results indicate that main peaks (the angles of 2θ) of NMO catalysts are turned up from 28.7, 37.3 and 56.8 to 23.1, 32.9 and 55.1 at the boundary of 500 C. As seen in TGA experiment, the NMO catalysts calcined beyond 500 C have mainly Mn_2O_3 phase. It is, therefore, considered that this phase-transfer causes NMO catalyst to decrease the activity of ozone decomposition. The specific surface area according to the calcination temperature is presented in table 2. The specific surface areas of NMO catalysts calcined below 500 C is almost identical to dried NMO catalyst. But that of the

NMO catalyst calcined at 700 C is deeply decreased. Finally the calcination over 700 leads to the release of lattice oxygen and then the shrinkage of micropores, sintering of NMO catalyst, showing remarkable decrease in the ozone decomposition activity.
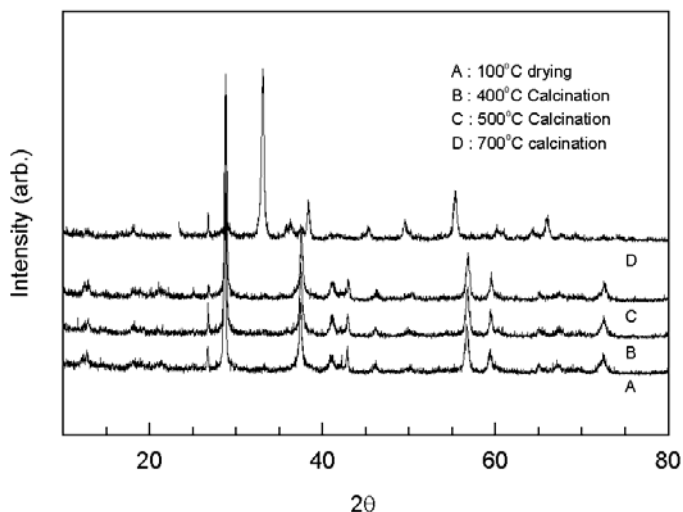

Figure 3. XRD patterns of NMO catalyst prepared at different calcination temperatures.

Table 2. The BET specific surface area of NMO with respect to calcination temperatures

Conditions	Fresh	100 C Drying	400 C Calcination	500 C Calciantion	700 C Calcination
Surface area $(m^2 g^{-1})$	32.2	31.2	30.2	28.8	14.2

Generally, the reaction of ozone decomposition happens onto the surface of catalysts. Therefore, it is very important to observe the surface composition of NMO catalysts according to the calcination temperatures. Fig. 4 is the result of the wide scan for a variety of calcined NMO catalysts. The analysis reveals the presence of impurities and some metals such as C, Si, Al and Fe. The amount of residual carbons decreases with increased calcination temperature. Specially compared with the intensity of O 1s orbitals, it was remarkably appears in NMO catalyst calcined at 400 C. Since oxygen onto the surface of NMO catalyst participates in redox reaction of ozone decomposition, it is conformed that the optimal calcinations temperature was 400 .
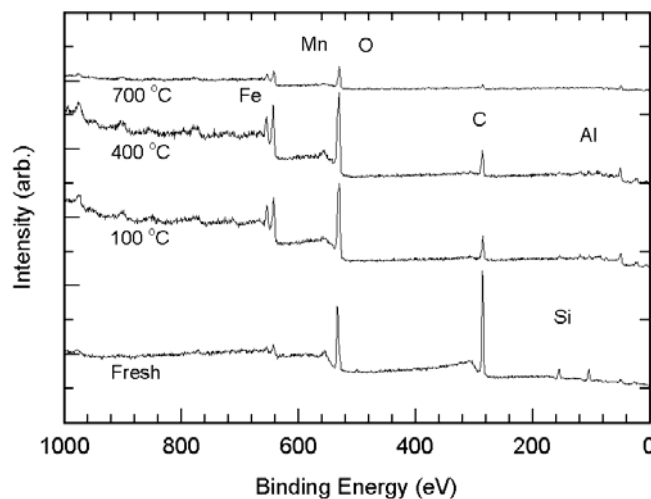
Figure 4. XPS wide scans of NMO catalyst prepared at different calcination temperatures.

Figure 5 shows the XPS patterns of manganese oxides in NMO with different calcination temperature.   The typical binding energy of MnO_2 and Mn_2O_3 is indicated in Table 3.   The binding energy of Mn $2p_{3/2}$ in fresh NMO appears at 642.3 eV, then being shifted to 641.4 eV as increased calcination temperature and also the binding energy of Mn $2p_{1/2}$ for fresh NMO and calcined NMO at 700   is 653.7 and 652.9 eV, respectively.   Thus it could be ascertained that the phase change from MnO_2 to Mn_2O_3 occurs as increased calcination temperature and results in low activity of ozone decomposition.

Table 3. The binding energy of manganese oxides

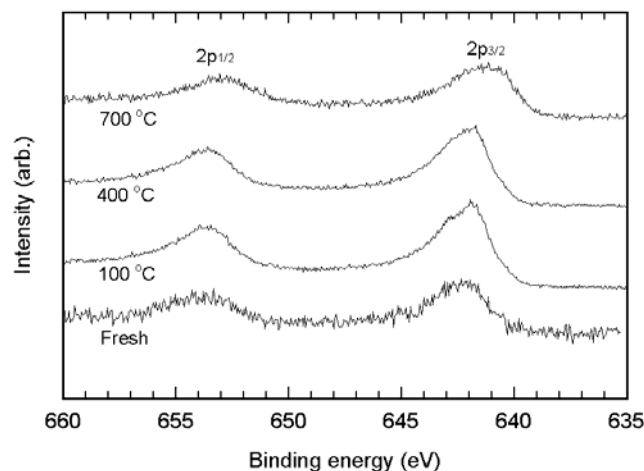| Type	$2p_{1/2}$	$2p_{3/2}$
MnO_2	653.9 eV	642.3 eV
Mn_2O_3	652.9 eV	641.4 eV

Figure 5. XPS narrow scans of NMO catalyst prepared at different calcination
temperatures.

To compare with manganese oxides in NMO, pure MnO_2 and $MnO_2/$ -Al_2O_3
catalysts are tested and the activities of ozone decomposition are shown in Fig. 6.
Physical properties of these manganese oxides are presented in Table 4. The pure
MnO_2 catalyst shows the highest ozone decomposition activity. In spite of high
surface area, MnO_2/γ-Al_2O_3 catalyst has very poor ozone decomposition activity. In
the case of space velocity is increased by 25,000 hr^{-1}, the activity of NMO catalyst is
similar to pure MnO_2 catalyst. Radhakrishnan, et al. (2001) suggested that the
desorption step is a reduction step which proceeds when electrons are transferred to
the manganese center by peroxide species to form oxygen. Therefore, it seems that
the reducibility of the manganese sites is crucible for the activity of ozone
decomposition.

Table 4. Physical properties of NMO and manganese oxides (calcined at 400 C)

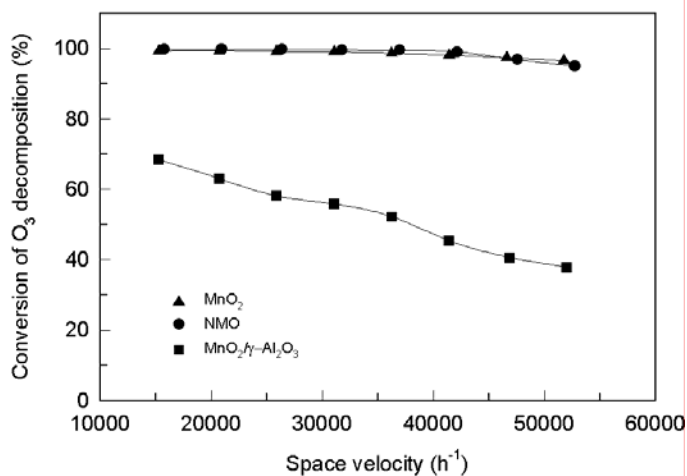| Catalysts	Surface area $(m^2\,g^{-1})$	Pore volume $(cm^3\,g^{-1})$	Average pore diameter (Å)
NMO	30.2	0.0398 (> 930 Å)	91.84
MnO_2	22.48	0.0479 (> 1130 Å)	98.41
Mn_2O_3	18.24	0.0404 (> 1040 Å)	95.32

Figure 6. The conversion of ozone decomposition as a function of space velocity for a various manganese oxides (calcination temperature = 400 C; inlet ozone concentration = 4.5 ppm).

TPR profiles of the NMO, MnO_2 and $MnO_2/$ -Al_2O_3 catalysts are shown in Fig. 7. Based on the fact that TPR up to 900 C leads to MnO formation, the average oxidation state of the metal could be determined from hydrogen consumption. In this study all samples also show two major peaks but $MnO_2/\tilde{\gamma}Al_2O_3$ exhibits one shoulder on the ending edge. MnO_2 reduces first in one step to Mn_3O_4 and in a second step to MnO.
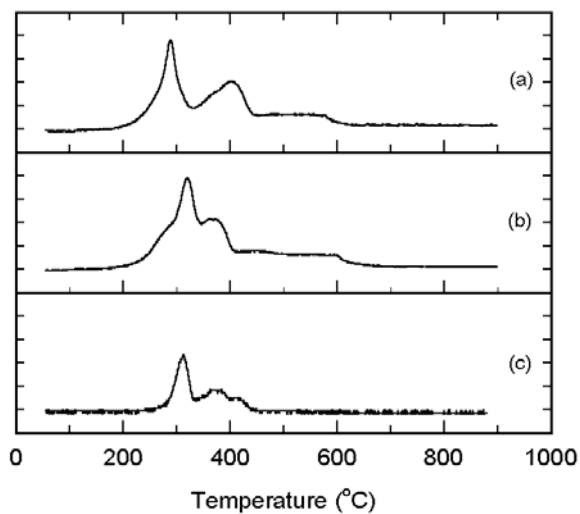

Figure 7. TPR profiles of manganese oxides (reducing gas; Ar 40 vol.% based H_2; gas flow rate = 50 ml min^{-1}; sample wt. = 50 mg, 10 K min^{-1}, (a) MnO_2, (b) NMO and (c) MnO_2/γ-Al_2O_3).

Therefore, the first peak indicates to change from MnO_2 to Mn_3O_4. And second peak indicates to change from Mn_3O_4 to MnO. The reduction ends exhibits green gray color that suggested MnO. The exact estimation of phase change of NMO is difficult because NMO is composed of various metal oxides. It is suggested that the first peak is to change manganese oxides because NMO contained manganese oxides mainly. The onset of reduction in TPR indicates the temperature of desorption of lattice oxygen for redox function. The onset temperature of reduction of MnO_2 and NMO is about 160 C, and that of $MnO_2/\tilde{\gamma}Al_2O_3$ is about 220 . In accordance with this fact we presume that the activity of MnO_2 and NMO exhibits higher than that of $MnO_2/\tilde{\gamma}Al_2O_3$. The hydrogen consumption ratio of MnO_2, NMO and $MnO_2/\tilde{\gamma}Al_2O_3$ from the first peak area is 1.0 : 0.93 : 0.44. The amount of lattice oxygen of MnO_2 and NMO is similar.

According to the reaction mechanism proposed by the studies of Mehandjiev, et al. (2001) and Rakitskaya, et al (1999), it can be concluded that the reaction intermediates of ozone decomposition should be the electron-rich species such as O^-. Since manganese oxides in NMO catalyst prepared in optimal conditions are almost in the oxidation state of 4, the probable mechanisms as follows:

$$O_3 + Mn^{4+} \rightarrow O^- + Mn^{3+} + O_2 \qquad\qquad (2)$$

$$Mn^{3+} + O^- + O_3 \rightarrow Mn^{4+} + 2O_2 . \qquad\qquad (3)$$

In the view of electron mobility, manganese oxides in high oxidation state hold a large number of empty d-orbitals which permits greater reducibility.

Presently, some catalysts experience a long-term decline in the activity of ozone decomposition. Higher activity as well as the development of lack deactivation is important goals in catalyst improvement. Heisig, et al (1997) investigated over a series of activated carbon-supported oxide catalyst. The study of binary oxide combinations formed from MnO_2, Co_3O_4, Fe_2O_3 and NiO shows a small decline in activity over time, so a real steady state could not be reached. Also Dhandapani and Oyama (1997) studied the activity over oxides of Mn, Co, Ni, Cr, Ag, Cu, Ce, Fe, V

and Mo supported on Al_2O_3. The decline in activity over all catalysts is analogous to that of carbon-supported oxide catalyst.

4. CONCLUSIONS

Natural Manganese Ore (NMO) is found to be very promising catalyst from the viewpoint of activity. The main component of NMO consisted of β-MnO_2 (pyrolusite), which could act as active site of ozone decomposition. The activity of NMO with respect to calcination temperature is observed. The preparation of drying could not remove the residual hydrated water but only remove the physical adsorbed moisture. This reason may deteriorate the catalytic activity and necessitates the preparation of calcinations. Increasing the calcination temperature of 400 results in decreasing the ratio of MnO_2 to Mn_2O_3, subsequently the catalytic activity. The activity of pure MnO_2 and γAl_2O_3 supported MnO_2 are compared with that of NMO. For space velocity below 25,000 h^{-1}, NMO shows the same activities as pure MnO_2 and the higher than MnO_2/γ-Al_2O_3. It appears to be correlated with the reducibility of lattice oxygen by TPR experiments.

5. ACKNOWLEDGEMENTS

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